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Economic Geology

and the Bulletin of the Society of Economic Geologists

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INTRIGUING EXAMPLES OF GEOLOGY APPLIED TO INDUSTRIAL MINERALS[1]

JOSEPH L. GILLSON

YOUR speaker has devoted his life to a study of the industrial minerals, specializing in a few but making broad general reviews of the whole field. He has noted that the dollar value of the industrial minerals produced in the United States stands, in relation to the dollar value of the metals produced, in the ratio of $3.2 billion for the non-metals to $2.2 billion for the metals (1957). When the metals and non-metals produced in this country are tabulated, it is found that 7 metallic ores exceeded $40 million in value, but that 10 non-metals produced have that gross value for that year. These are: iron ore, copper, zinc, lead, uranium, gold, and molybdenum; stone, sand and gravel, cement, clays, salt, sulfur, lime, phosphate, potash, and bromine.

Your speaker must point out a fact that has probably occurred to you that the list of non-metals includes cement and lime, which are essentially manufactured products rather than crude ores, and if cement and lime are eliminated, the comparison between the two in total is nearer a 50-50 ratio; also that the list of metals does not include iron and steel and aluminum and other finished metals in the quoted total of $2.2 billion.

When it comes to plain bulk, it is interesting to point out that the tonnage of crushed stone, and of sand and gravel, each exceed the tonnage of all of the metallic ores produced, and even exceed the tonnage of solid fuels.

In spite of this large volume and dollar value of the industrial minerals produced in the United States, the industry has not attracted any large number of men in the geological profession to engage in it, nor to write about the occurrences.

I have no figures on the number of geologists who are spending a major proportion of their professional time in the industrial mineral field, but I suspect that the number is less than 100, or roughly ten percent of the membership of our society. Judging by publications in Economic Geology, a

[1] Presidential address delivered before the Society of Economic Geologists, New York Meeting, February 18, 1960.

tabulation for the years 1949 to 1958, inclusive, showed that there were 52 lead articles dealing with industrial minerals out of a total of 482, or about 11 per cent. There ought to be many more opportunities for men to work in the industrial minerals field than in the metals field. Of course there are other circumstances that militate against the use of geologists by companies producing industrial minerals. Many producers have not yet felt a serious pinch in reserves and have not needed geologists to find them.

It is certainly not any lack of stimulating geological problems offered by the occurrences of the industrial minerals. Having just completed an assignment as editor of the new edition of "Industrial Minerals and Rocks" which has just been published by the AIME, your speaker has had a chance to review summaries from a very large number of recent articles describing the broad field of industrial minerals. A selection of some of the outstanding problems, mostly geological, but also mineralogical and chemical, is the subject of this paper, presented in the hope that these stimulating problems will attract more men into this field.

These will be reviewed alphabetically. Naturally the selection of the subjects reviewed is a very random one, based only on a selection of subjects that seemed of especial interest to the writer, and that can be covered within the time limitations of this presentation.

ASBESTOS

Although many fibrous minerals, both natural and artificial, are known, the almost unique properties of serpentine asbestos make it a subject of outstanding scientific and commercial interest. Until a synthetic mineral is made, and that is yet possible, that is both more refractory than serpentine asbestos and even more flexible, permitting spinning without blending it with some flammable organic fiber as is now practiced in asbestos cloth, then our industrial dependence upon this mineral must continue.

The first striking thing about asbestos is the restricted number of commercial occurrences. The bulk of it comes from only three areas in the world—the eastern townships of Quebec, the Bajenova district of the U.S.S.R., and from several places in southern Africa. Nearly half of the world production comes from ten deposits in a belt only 55 miles long, in the eastern townships of Quebec, associated with ultrabasic intrusives. Nevertheless, similar ultrabasic rocks, more or less completely serpentinized, are found in a long belt extending down to Alabama, as was pointed out by Hess (28).

Yet except for one deposit in Vermont, none of these serpentines in the United States carry any commercial asbestos. There seems to be specific reason why each one of these ten deposits in the eastern townships of Quebec is located where it is. Quoting Jenkins (33):

> Major faults, along with subsidiary faults, have evidently played an important part in localizing the formation of the asbestos deposits in the Eastern Townships. Irregularities in the peridotite contact were in some instances responsible for the form and distribution of these faults. Serpentinization, caused by the introduction of the swarms of small acid intrusives, influenced the formation and configuration of the subsidiary faults, and where these intrusives were large they probably tended to trap the vein forming asbestos solutions.

Riordon (54) thinks that colloidal serpentine was first deposited in the veins, and this crystallized later to form picrolite, a splintery form of serpentine. Chrysotile asbestos was derived from the picrolite of the preformed composite veins, as a result of recrystallization during the cooling stage subsequent to the formation and primary crystallization of these veins.

In commenting upon Mr. Riordon's ideas, D. H. James (32) noted that numerous two-fibre veins, when separated along the median parting, reveal a botryoidal surface of low relief on the thicker portion. This feature supports the idea of formation as a colloidal gel in fractures. Mr. James says that high temperatures have not been demonstrated to be the major controlling factor in asbestos genesis.

The importance of colloids in mineral formation was stressed 35 years ago by Lindgren (40, 41, 42) and by Boydell (3). Lindgren stated that gels and colloid precipitates often harden to rounded reniform masses referred to as "colloform." A further observation on colloidal solutions will be made a little later when discussing fluorspar. Lindgren pointed out that solidified colloids have a tendency to acquire crystallinity and may become transformed into fibrous or cryptocrystalline aggregates.

In Arizona serpentine occurs in metamorphosed limestone in contact with intrusive diabase sills. In Arizona, Stewart (58) says that the asbestos occurs in bands of serpentine in the Mescal limestone of Precambrian age which is intruded by diabase sills. Diabase sills in limestone are very numerous, but serpentine is not a common "contact metamorphic" mineral in such associations—in other words the rocks exuded magnesium, possibly almost exclusively, only magnesium seems to be an unusual abundant ion in such solutions.

In South Africa two varieties of amphibole asbestos, crocidolite and amosite, occur in banded iron stones, which are described as iron-rich silicified argillites. In some places sills of dolorite are interbedded in the banded iron stones. However, for these amphiboles to form, there must have been an introduction of magnesium in the case of amosite, and of sodium in the case of crocidolite.

A great deal of work has been done in many laboratories in an attempt to make synthetic asbestos, or some other fibrous compound which would have a higher melting point than serpentine asbestos, and perhaps be more flexible. A review of some of the early work and tests conducted at Norris, Tennessee, has been given by Comeforo and Kohn (13, 13A, B). Potassium titanate, aluminum oxide and various glasses have been made fibrous. Fiber glass, fibrous silica and fibrous aluminum silicate glass have developed into very useful products, but they have not replaced natural asbestos yet, and seem to have a long way to go to do so.

BARITE

This mineral turns up in all sorts of places and in a variety of associations. An explanation of its widespread occurrence as disseminated grains in limestone was pointed out by Dunbar and Rodgers (16). Barium and strontium cannot substitute for calcium in the calcite structure, but can enter the

aragonite structure. Aragonite appears to be the form of calcium carbonate normally produced by precipitation from sea water. Barium would be expelled on the subsequent conversion of metastable aragonite to stable calcite. In the presence of almost universal SO_4 ions, barite would form, thus accounting for the scattered crystals of barite so common in sedimentary rocks.

The other facet of interest about barite is its occurrence as an almost complete replacement of large masses of sedimentary rocks, as in Nova Scotia, Nevada, and in Germany at Meggen. It also occurs in many type of veins, and is an associate of rare earth deposits such as the one at Mountain Pass in California and at Araxá in Brazil. The intriguing thing about these deposits is the amazing concentration of this one metallic ion, which is a very minor constituent of most igneous rocks, and of ore-bearing veins, of volcanic emanations, of natural brines, and of sea water. It is reported in the analyses of some chloride waters by Clarke (11), but it seems to be much less frequently reported in natural brines than is strontium. Although large deposits of strontium sulfate are known, they are not anywhere near as widespread, nor individually so large as of barite. Tenny (53) ascribed the source of barium found in the Walton, Nova Scotia, deposit to rising connate waters (which means original sea water) whereas Ehrenberg and associates (17) credited submarine igneous emanations with supplying the barium for the Meggen deposits in Westphalia. The deposit of celestite at Ludlow, California, is obviously a playa in which the celestite is interbedded with volcanic ash. There volcanic emanations must have been the source of the strontium ion.

Exploration for residual barite deposits by gravity survey were reported to have been successful in the Missouri field by Uhley and Scharon (64).

BORON

Boron and its compounds has been much in the news lately due to a short-lived enthusiasm for some rocket fuels made from the highly toxic boranes. Those residents of states served by oil companies that use an unspecified boron compound in refining high octane gasolines are told by various radio announcers daily that gasoline must be better, since it has boron in it. Cubic boron nitride, a synthetic crystalline substance about as hard as diamond, has also attracted much publicity, and may become a widely used abrasive. However, the consumption of boron compounds, which has gone up very rapidly since 1930, is still dominantly in ceramics, in glass, and in soaps and other detergents.

The geologist studying Californian borate deposits finds himself involved in the glacial history of two ice ages in the Sierra Nevada called the Tahoe and the Tioga, and studying the elaborate drainage system in the Owens Valley, the headwaters of which are near the Mono Craters volcanic field. Searles Lake was a final settling basin where the evaporation is high. Although Owens River is fresh water and carries only 1 ppmm of boron, nevertheless it does carry about 800 tons of B_2O_3 per year, which is enough to account for the accumulation in Searles Lake.

The hydraulics and solid accumulation of Searles Lake is relatively easy to understand, and the source of boron from volcanic waters is acceptable. White (66) says that a high boron-chloride ratio (as in Searles Lake), is usually an indication of volcanic water.

The immense quantity of sodium borate at the deposit at Kramer is quite a different subject, and one much more difficult to understand. A reserve of 100 million tons of borax and kernite ore is found in Pliocene beds at depths of 150 to 1,000 feet below the surface. The host material is lacustrine, found in faulted and tilted beds. According to Smith (60), the sediments were deposited in the quiet waters of a rather deep lake. The kernite which is the sodium borate with four molecules of water, is found in the lower part of the ore body, and much of it is in large crystals, a foot or more in size. The cross-cutting relationships of the kernite to the bedding shows plainly that kernite is a secondary mineral, but the conditions under which it formed are not agreed upon.

A second series of lake-bed sediments lies above the sodium borate ore, and it contains different borates, including magnesium borates in a basal layer with ulexite and colemanite above. There is evidence that a sodium borate section and other soluble minerals were removed, since saline minerals that normally accompany borax are lacking in the Kramer deposit. Nevertheless the extraordinary quantity of sodium borate almost free from other salines is difficult to understand.

Recent drilling east of Kramer by the U. S. Geological Survey has developed a large tonnage of low-grade colemanite in beds similar to those overlying the sodium borate section at Kramer. This discovery encourages exploration in other basins in the general desert area that are covered with alluvium. More exploration may explain the Tertiary history of the region.

BROMINE

A mineral raw material that is produced to the value of fifty million dollars per year ought to be widely recognized and identified as one of the more important members of the mineral industry. Instead of that, bromine has been almost ignored, or classed among the "minor minerals." It is used in anti-knock formulations that are added to gasoline under the general name "ethyl gas"; the compound is ethylene dibromide. Most of it is recovered from sea water, which according to Rankama and Sahama (53) carries 65 parts per million. Some oil field brines carry a great deal more, especially the El Dorado field in Arkansas. D. E. White (66) cites an analysis of a well in Elliot County, Kentucky, with 870 parts per million, and it is understood that a number of wells in Alberta have been found recently to carry substantial quantities of bromine. Clark cites wells from Pomeroy, Ohio, and Hartford, West Virginia, with high Br. The water in the Dead Sea is reported to carry 100 times as much bromine as sea water. According to Clarke (12) the saline residue from the Dead Sea analyzes from 1.55 to 2.72% Br. Apparently no other salt lakes have anywhere near this quantity of Br. Volcanic waters and emanations are low in it.

CLAYS

A lawyer friend of mine once told me gloatingly how he had discredited the testimony of a geologist posing as an expert in a case on which he was the opposing attorney by asking the expert the question, "What makes clay slick?" The man didn't know. If the speaker had been called upon under such a circumstance, he would have replied that "clays adsorb water which acts as a lubricant." A little better, but still simple explanation is given by Longwell, Knopf and Flint (43) in their textbook on geology.

> To its content of flaky minerals and the specific properties of the interstitial water, which acts as a lubricant, clay owes its most characteristic and supremely important technological property—its plasticity, by virtue of which it can be molded when wet into any desired shape, and will retain this shape on drying.

No modern definition that your speaker can find serves simply. Grim (21) said:

> The activity of a soil material is defined as the ratio of the plastic index of the fraction finer than two microns. The plastic index is essentially a measure of the water holding capacity of the clay between the amount required to develop plasticity and the amount necessary for flowage.

In another reference Grim (18) wrote:

> Students of clay have long recognized that an understanding of the plastic properties of clays is based on an understanding of the character of the water in clay-water systems, the nature of the binding force between individual clay mineral particles and the factors that control the character of the water and the nature of the binding force.

When the first edition of the volume INDUSTRIAL MINERALS AND ROCKS was published by the AIME in 1937, the chapter on clays was written by Prof. Heinrich Ries of Cornell who had devoted a lifetime to the study of clays and was one of the recognized authorities in the field. In his chapter there is no mention of sheet structures with layers of silica tetrahedrons and alumina octahedrons, expanding lattices and exchangeable cations. Plasticity was defined by him as follows:

> When a clay dries from its plastic condition to a constant weight at room temperature, the water that evaporates until air shrinkage ceases is known as "shrinkage water." That which is still left in the intergrain spaces is termed "pore water" and may be driven off at 110° C. The pore water and shrinkage water together are known as the "water of plasticity."

That hardly explained plasticity. That water could enter between the sheets in the lattice was not appreciated until X-ray defraction methods and the electron microscope was put to work studying the internal structure of clays. Thanks to the work of Grimm (19, 21), Ross and Kerr (55, 56, 57), Bradley (5, 6), Brindley (7), annual symposia (47) and clay conferences (48), our knowledge of the actual nature of clay minerals and the reasons for their unique properties has increased greatly.

To the surprise of some of those like myself trained in an earlier day, minerals like chlorite and vermiculite turn out to be clay minerals, rather than

members of the mica group. Bentonite, which has been known to be a variety of montmorillonite, was known to vary chemically and in its applications. The Wyoming bentonite which is a sodium bentonite expands in water, and is useful as a drilling mud, but not in colorizing or in making catalysts. Calcium bentonites from Mississippi and Texas are good for decoloring and foundry use, but not for drilling muds.

The nature of the bleaching action of a calcium montmorillonite was explained by Kiersch and Keller (39) who described an Arizona deposit.

All of this very erudite study of the crystal structure of the clay minerals still does not describe the geological occurrences, nor evaluate reserves. It is for that reason that detailed geological studies like that of Kesler (37) on Georgia and South Carolina kaolin are so instructive and helpful. Similar work by Wisser and Turner (67) on California clays, and by Manz (45) on those in North Dakota are examples of other descriptive reports.

FLUORSPAR

Fluorspar has been a mineral with which I have been concerned for many years. In general, fluorspar is a lone wolf, occurring in deposits that are away from mining districts noted for the occurrence and production of other commercial minerals, although in places it is associated with barite and celestite and a few deposits carry enough galena, and a few others enough sphalerite so that production of these sulfides is an important factor in the economics of the operation. Fluorspar veins are being worked in the old lead mining district of the Black Forest in Southern Germany, in old lead districts in England, and there is so much fluorspar in the gangue with the copper-lead-zinc deposits in the Parral district of Chihuahua in Mexico that serious planning is now under way to recover the mineral from the tailings of the sulfide flotation plants.

In most fluorspar deposits, however, no other economic mineral occurs in the ore, nor are there any other mines of other minerals anywhere nearby. In many districts no igneous rock is exposed near the fluorspar deposits, and in others where there is some igneous rock in the district, no obvious relationship exists between them. Lindgren (41) pointed out that fluorspar is a persistent mineral and formed at all temperatures. Grogan (22) studied the fluid inclusions in crystals of fluorite from Southern Illinois and concluded that the temperature varied from 85° to 120° C.

Crystals of fluorspar have been found in the Santa Anita district of northwestern Coahuila with bubbles of asphalt inside them. These suggest a very modest temperature of formation.

Peters (52) made a thorough study of a large number of fluorspar deposits in the western United States and has done more thinking and philosophizing about the formation of fluorspar than perhaps any other recent student.

Dr. Peters has prepared a somewhat fanciful but thought-provoking diagram on the geochemical cycle of fluorine. He points out that there are contact pyrometosomatic deposits, in which fluorite is associated with high-temperature silicates; then hypothermal veins in which fluorite is the gangue

with tungsten and tin mineralization; then mesothermal veins, and finally epithermal ones. In nearly all of the deposits of commercial size that the speaker has examined, all of the evidence points to the probability that a fairly low temperature existed at the time of deposition.

D. E. White (66) reported that fluorine is relatively high in springs of the sodium chloride type and attains concentrations as high as 20 ppm in alkaline waters with little calcium. Even though the volcanic sodium chloride waters are high in fluorine, some volcanic gases have higher F/Cl ratios; this suggests that much has been fixed at depth as fluorite or in silicates such as the micas.

In another paper (65) the same author describes hot springs that are or have deposited fluorite, including Ojo Caliente in New Mexico, Poncha Springs, Colorado, Wagon Wheel Gap, Colorado, Browns Canyon, Colorado, and Bruffeys Hot Springs, Nevada.

Iin many deposits some at least of the fluorspar was deposited in open cavities. The strong tendency for the mineral to grow into well formed cubic crystals has resulted in the finding of many beautifully crystallized masses, some with cubes six inches or more across. The formation of fluorspar in mammillary and concentric growths has been noted in various places, as for instance in Browns Canyon near Salida, Colorado, mentioned above, and especially in the San Vicente district of northern Coahuila. There big masses are found now embedded in clay, but between limestone walls that are fresh and hard. These rounded and mammillary masses look like agate or cave onyx. It is suggested as a speculation that the fluorspar started to grow from a colloid, which has subsequently crystallized. When broken, the masses seem to have a radial crystal structure which is striking, since it formed from an isometric mineral.

A quotation from Lindgren (41) was given above, stating the colloform masses formed from colloids acquire crystallinity and may become transferred into fibrous or cryptocrystalline aggregates.

Peters quotes Lindgren in ascribing a geographic distribution to fluorspar deposits in the western United States. He noted that fluorspar deposits are relatively uncommon in the Pacific States, and most abundant along the eastern Rocky Mountain front where they are associated with alkalic rocks. This observation permits speculation on the association of fluorspar with regional magmatic differentiation, resulting in earlier intermediate magmas in the west, which did not release fluorine and later alkalic and felsic magmas along the eastern margin. Unfortunately for the theory, a considerable number of important fluorspar deposits have been found since Dr. Lindgren's time; in Nevada, Utah, Idaho and Western Montana, although still none of importance in California.

Fluorspar occurs with remarkable frequency in Mexico and in the Western United States with rhyolite, either in veins cutting flows, or in limestone in contact with rhyolite, or in rhyolite in contact with limestone. Scores of other examples can be given where fluorspar occurs in Precambrian or early Paleozoic granites or diorites.

There are two deposits in Mexico that should be examined by every geologist who thinks he has seen everything, since these are most unusual, if not unique.

The first of these is the Azul mine and its neighbor, the Gavilon mine, located near Taxco in the State of Guerrero. These deposits are more or less circular in plan, and the fluorspar is a replacement of limestone fragments, big and little, in a matrix of altered volcanic ash. The surrounding limestone is hard and unaltered. An explanation that at least fits some of the facts, although "doubting thomases" have objected to this conclusion, is that this was a sinkhole in the surface of the Cretaceous limestone in pre-Miocene time. The sinkhole was filled with volcanic ash which sifted in around the big and little blocks of limestone that lay in the sinkhole. The volcanic sequence continued for some time and later fluorine solutions found the buried sinkhole an easy place to circulate. The solutions replaced the limestone chunks but did not find the hard limestone walls amenable. Erosion of the volcanics down to the old limestone surface exposed the deposit.

The other deposit is in Northern Coahuila, close to Stillwells Crossing of the Rio Grande. It has been described briefly by McAnulty (44) and is called the Agua Chile deposit. This consists of a crater-like rim, surrounding a spine of syenitic rock that is thrust up in the center of the collapsed core. A rhyolite sill was intruded in the Cretaceous limestone and crops out all around the inside of the pseudo "crater." The fluorspar occurs in the limestone just below the rhyolite. The association of fluorspar in limestone in contact with rhyolite is characteristic of the district and hence there is nothing particularly striking about the actual occurrence itself, but the geologic setting in the rim of this pseudo-crater is certainly something to see, and is a most favorable factor from a mining point of view, since a great deal of the deposit is accessible to open pit operation.

LIME AND POZZOLAN CEMENT

In the preparation of the chapter on lime in "Industrial Minerals and Rocks," I as Editor raised some questions with a statement made by the authors, who are technical people long experienced in the lime industry. In discussing that important new use for lime in soil stabilization of road bases and sub-bases, the authors (4) stated that

> Lime is effective particularly with clay soils in reducing plasticity, shrinkage and swelling characteristics. A complex cementing action, which highway soils experts regard as largely pozzolanic, also occurs in varying degrees, which adds compressive and fluxural strength to the road base.

I found that I had to learn a little about that action that is described as pozzolanic. Fortunately a study of the subject was made recently by three authors writing in Economic Geology for 1951 (46). The following is summarized from their paper:

> During the Greek and Roman periods, calcined limestone was employed either alone with water or mixed with sand and gravel or crushed stone, tile or brick. With some experience the ancient engineers observed that some aggregate materials

produced mortar and concrete which were stronger and more durable and which hardened as well under water as in air. These aggregates were volcanic ashes and tuffs. They included Santorin earth, a rhyolite tuff from the island of Santorin, and the phonolitic tuffs in the vicinity of Vesuvius, particularly from deposits near the town of Pozzuoli, from which locality these materials derive their name—pozzolan.

With penetration of the Romans in western Europe, similar volcanic ashes and tuffs were found and used in southeastern France and subsequently along the Rhine River between Cologne and Coblenz. The Romans discovered too that ground tile, pottery and brick would serve as pozzolan, and these were used where volcanic pozzolans were not available as in England. Similar use of gound brick is made today in India and Egypt.

Natural pozzolans owe their chemical activity to one or more of five substances: (1) volcanic glass, (2) opal, (3) clay minerals, (4) zeolites, and (5) hydrated oxides of aluminum.

Artificial pozzolans, including fly ash, ground brick, burned oil shale, owe their chemical activity to glasses produced by fusion of the ingredients in the original material.

Among the natural pozzolans, in addition to the volcanic glasses and tuffs, the following common material are included: diatomaceous earth, kaolins, bentonite clays, fullers earth, glacial clays, Attapulgus clay, and bauxite.

In California, the Monterey chert was used as an aggregate in the Golden Gate and San Francisco bridges, the Puente chert in Davis dam, the Rosamond tuff in the Los Angeles aqueduct, and bottom sediments from San Francisco Bay were used in Bonneville dam. In these uses, of course, ordinary cement was used in addition to the pozzolans.

All clayey pozzolans must be calcined at temperatures over 1000 degrees F. to induce optimum activity and to reduce water requirements. Except for some exceedingly fine grained pumicites in California and Texas, all natural pozzolans require grinding to develop fineness sufficient to use for a cement mixture.

No one yet seems to have identified the mineralogical changes that take place when lime reacts with volcanic glass, opals, clays or bauxite. The setting of ordinary mortar is simple carbonation—the $Ca(OH)_2$ reacts with the CO_2 in the air and becomes $CaCO_3$. Presumably the reaction between lime and glass or lime and opal is the formation of some calcium silicate that hydrates to a hard crystalline compound. With clay or bauxite, it must form a calcium aluminate, as in portland cement.

PEGMATITES

No review like this of interesting geological and mineralogical features can overlook the pegmatites. However, it is almost impossible to pick out one or two outstanding examples of interesting geology, since every phase of the subject is a fascinating one. A major emphasis should be made on the tremendous amount of study and reporting that has been done during the past fifteen years. To mention only a few names, there are Jahns (*29*, 30, 31), Heinrich (*24*, *25*, *26*, *27*), Griffits, Olson (*26*), Cameron (*9*, *10*), W. D. Johnston (*35*), Bhagwar Das (*34*), Duncan Derry (*15*), L. R. Page (*49*), W. T. Pecora (*51*), and R. B. Rowe (*59*).

If there is one outstanding contribution of these extensive studies, it may be zoning. According to Jahns, the careful mapping of zonal structures began

about 1940, although zoning was recognized by Grout (23) over 20 years before.

In the monograph on Internal Structures of Granitic Pegmatities (10a) the following zones are recognized by the men in the U. S. Geological Survey who did most of the studies, between 1940 and 1950:

> Zones, i.e., successive shells, complete or incomplete, that reflect to varying degrees the shape or gross structure of the pegmatite body. These zones are:
> A. The outermost or border zone.
> B. The wall zone.
> C. The intermediate zone, or zones.
> D. The core, or innermost zone.
> In addition to these zones, there are fracture fillings that fill fractures in previously consolidated pegmatite and replacement bodies, which are units formed essentially by replacement of pre-existing pegmatite.

Most of the many references cited above describe and have pictures and diagrams of scores of examples, and of great variety.

A regional zoning was first noted by Brögger (8) and many examples have been cited by Heinrich (25). A typical example is in the Yellowknife District described by Rowe (59) who stated that the pegmatites found away from the granite can be classified into five zones; the first zone contains large irregular shaped pegmatites that have poorly developed internal structure, and contains beryl. The third zone contains many pegmatites that have beryl as a component but no graphic granite. The fourth zone contains pegmatites that are similar structurally to those in the third, but many contain columbite-tantalite as well as beryl. The fifth zone, farthest from the granite, features pegmatites that carry spodumene.

The recent growing demand for lithium ores has led to the study of many of the pegmatites containing lithium minerals, principally by Page (49), Derry (15), Rowe (59) and Kesler (36, 38). The largest resources are in the Carolinas in what is called the Kings Mountain District in a belt 25 miles long. Many of the pegmatites average 15 to 20 percent spodumene. It is an unusual feature of pegmatites that they could be that uniform; in fact zoning is said to be rare or poorly defined in them.

It is interesting that the lithium mineral petalite is a rarity in North America, but is one of the common minerals in the lithium-bearing pegmatites of Southern Rhodesia, Southwest Africa, and in Sweden.

SAND AND GRAVEL

It seems difficult for many people to realize that the production of sand and gravel is part of the mining business, and that together they constitute the mineral raw materials of largest volume produced in the United States. In 1958, the tonnage of sand and gravel (including industrial sand) produced was 680 million tons; the next competitor was crushed rock of which nearly 533 million tons were produced. Coal, both bituminous and anthracite, accounted for only 431,617,000 tons in the same year. Our coal friends will insist that 1958 was a year of low production, but sand and gravel have exceeded coal now for several years.

Also, the economic geology of sand and gravel deposits apparently is of no interest to the readers of Economic Geology. I had to go back to 1944 to find a paper by D. P. Krynine, the well-known engineering geologist, on Some Engineering Aspects of River Sand. There was a paper in 1949 on some glass sands in New Jersey, and one in 1946 on sands as an aquifer for Louisville water supply. Economic geologists are interested in sands only if they have some gold, diamonds, or ilmenite in them.

In a preceding section the voluminous literature on pegmatites was mentioned. It is probable that the total dollar value of all of the feldspar, mica, quartz, beryl, lithium and rare minerals that have been produced from pegmatites in the United States from Colonial times will not equal the current annual value of sand and gravel. Yet, except in some state reports, which are very thorough, the literature on sand and gravel is quite minor.

As a matter of fact, the geology of sand and gravel deposits is exceedingly interesting, and becoming of very real importance because of the tremendous use in building, highway, and dam construction. The fact that our cities have spread out into the suburbs and surrounded sand and gravel pits that had been in operation for decades, and the zoning laws were invoked to shut down the pits, has driven the operators out in the country seeking new sources of supply. In the northern states where glacial deposits exist or there are outwash aprons and gravel trains, many alternative sources of supply exist, and ample deposits can be found in the Mountain states. In the Southern states, however, deposits of coarse aggregate are rare, and around many cities it is necessary to ship gravel for a hundred miles.

Good building sand itself is not found everywhere. The requirement that at least 20 percent must be retained on a 16-mesh screen eliminates many deposits because not enough coarse sand is found in them.

Delta deposits in old glacial lakes are sought in the upper tier of our states and of course other glacial features like terminal moraines, eskers, and kames are excellent sources of gravels. Further south, terrace deposits, both river and marine, are likely sources of supply, and are found by diligent studies of aerial photographs, and by geophysical methods of prospecting. Resistivity methods have been used for outlining sand and gravel deposits for twenty years, and have been very successful in a number of instances.

TITANIUM DEPOSITS

Your speaker has been investigating titanium deposits for about thirty years and has visited titaniferous magnetite, deposits of ilmenite-hematite; rutile deposits in rocks of various kinds; sand deposits varying in character from stream to marine and in age from Cretaceous to recent. He has written several papers on the occurrence of titanium oxides, both in rocks and in sands. At least so far, he has heard from no one that has taken serious issue with him on his ideas of the formation of sand deposits, but he seems to be almost alone in his ideas that rock deposits of ilmenite were formed by replacement.

In the new edition of "Industrial Minerals and Rocks," Mr. Lynd (43A)

of the National Lead Company described the very large deposit of titaniferous magnetite in the Adirondack Mountains of New York state, and discussed the various modes of origin that have been ascribed to it. It is this rock that in the speaker's opinion started out as a coarse grained anorthosite with very large crystals of labradorite. A soaking of the rock by more sodic solutions converted a great deal of the labradorite to a mosaic of fresh and clear andesine. Corroded large "phenocrysts" of labradorite remain in the ground mass of recrystallized andesine. This is considered by others just to be a porphyritic variety of anorthosite. Then, in the speaker's opinion, iron, magnesium and titanium solutions were introduced, and in places a metagabbro was formed, which nevertheless still retains these ghosts of the large labradorite "phenocrysts." As more and more iron and titanium was carried in, ilmenite and magnetite were formed, both in the anorthosite and the metagabbro. The ore still carries these ghosts of labradorite phenocrysts, much corroded, but still numerous.

Mr. Lynd made courteous reference to the ideas of the speaker, but then emphasizes that the majority of opinion among geologists that have studied the area favors some form of magmatic processes to account for the deposits. The most convincing of these, wrote Mr. Lynd, suggests that the original magma was a gabbroic anorthosite, which by fractional crystallization and "filter-pressing," or draining of the heavy liquid separated into semi-solid anorthosite and a gabbroic residual liquid.

These ghosts of original labradorite and abundant and ubiquitous evidence that the ore minerals were introduced late and have all of the long recognized features of late generation mineralization are convincing evidences of replacement in the speaker's opinion. This idea of "filter-pressing" never seems to die, and is repeated over and over again by people that don't seem to want to sit down and look at the rocks in the field with a hand lens, or the sections under the microscope. Fortunately for the operators of the mine, there is plenty of ore available, and the future of the mine does not depend upon the academic theories of "long-haired" geologists.

A similar difference of opinion exists in regard to the ilmenite-hematite deposits at Allard Lake, north of Havre San Pierre in eastern Quebec, and at St. Urbain, in County Charlevoix, Quebec. The speaker is convinced that they are pneumatolytic replacement deposits whereas most others who have examined them are satisfied that they are magmatic. Your speaker notes with some amusement that features which in the case of sulfide minerals are recognized as replacement textures are ignored, and the oxide minerals are called magmatic, apparently because they are oxides, and oxides are supposed to be magmatic.

Surely if we didn't have differences of opinion, our science would not have the zest that it does.

An interesting fact about the deposits at Allard Lake is that the magnetic anomaly is strongly negative. This was reported by Weston Bourret (2) who believes that the strong negative anomalies result from the effect of negative polarization of the orebody itself.

CONCLUSION

Obviously one could continue for hours citing interesting examples of geological and mineralogical features of deposits of industrial minerals. I hope, however, this random selection of a few examples that have interested your President, will whet your interests to investigate many others.

E. I. Du Pont de Nemours & Co.,
Wilmington, Delaware,
February 24, 1960

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ISOTOPIC COMPOSITION OF LEAD AND PRECAMBRIAN MINERALIZATION OF THE COEUR D'ALENE DISTRICT, IDAHO[1]

A. LONG, A. J. SILVERMAN, AND J. L. KULP

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ABSTRACT

Galena samples representing the vertical and geographical extent of the Coeur d'Alene mining district have been isotopically analyzed for lead. The isotopic composition is essentially uniform at $Pb^{206}/Pb^{204} = 16.44$, $Pb^{207}/Pb^{204} = 15.58$, $Pb^{208}/Pb^{204} = 36.52$. The common lead age from this average is about 1,400 million years. This is consistent with other isotope data in the district and may be considered the time of primary mineralization. The original Belt Series and its metamorphic equivalents are, therefore, older than 1,400 m.y.

Precambrian lead in veinlets cutting Laramide monzonite dikes and stocks present positive evidence for sulfide remobilization in Tertiary time in the vicinity of these igneous intrusions. Some minor rock lead was also introduced as galena during this event.

INTRODUCTION

THE Coeur d'Alene mining district in northern Idaho (Fig. 1) has been, for over eighty-five years, one of the most productive lead, zinc, and silver sources in the United States. The deposits are primarily replacement veins and are almost completely contained in the Belt Series of sedimentary rocks.

[1] Lamont Geological Observatory Contribution No. 409.

FIG. 1. Coeur d'Alene District, Idaho, and the Sullivan Mine, Kimberley, B. C.

It has been generally accepted (19, 28) that the ores are genetically, and in some cases spatially related to silicic intrusives that lie in the Laramide tectonic belt and which were recently dated by Larsen et al. (15) using the lead-alpha method at approximately 100 m.y.

Recent isotopic studies, however, have indicated that the pitchblende from the Sunshine Mine was deposited at least 1,200 million years ago (13) and that galena in the same mine (2) was deposited at the same time. It appeared worthwhile to examine this matter further, particularly to see whether or not all the Coeur d'Alene ore was Precambrian. By critical sampling it would be possible to detect systematic isotopic variations that might shed light on the origin of the deposits.

A suite of galena samples was collected and analyzed with the following specific questions in mind:

1. Is there any systematic horizontal or vertical variation in lead isotope composition within the district?
2. Which areas, if any, were mineralized during the Laramide disturbance?
3. What bearing do the lead isotope compositions have on the time and mode of mineralization of the ores?

GEOLOGICAL SETTING

Stratigraphy.—The youngest stratified rocks in the region are metasediments of argillites, quartzites, and calcitites of the Precambrian Belt Series as defined by Ransome and Calkins (19).

Low-grade regional metamorphism (presumably in Precambrian time) produced phyllites, quartzites, and marbles, but the primary sedimentary structures are still distinct. Hydrothermal alteration has been extensive around many of the ore bodies; sericitization, silicification, minor carbonatization and chloritization are most common. Alteration is discussed by Mitcham (17).

The igneous rocks of the Coeur d'Alene are all intrusive and range in size and shape from small stocks to dikes. The stocks outcrop north of Wallace, Idaho, and the Osburn fault. The range in composition from diorite to monzonite to syenite is analogous to the rock types in the Idaho Batholith. Numerous lamprophyre and diabase dikes also cut the metasediments. Small monzonite dikes are known in areas near the stocks.

The basic dikes appear to have occurred after the mineralization in the district (V. C. Fryklund, private communication). In some localities lamprophyres are known to cut off ore structures. There is, in a number of localities, a close spatial relation between sulfide mineralization and the basic intrusions, but this need not connote any genetic relationship.

Structure.—A complex pattern of folding and faulting is present in the Coeur d'Alene district (Fig. 2). The general fold pattern shows broad northwest to northeast trending folds north of the Osburn fault, and tight, northwest to east-west striking folds, some overturned to the north, south of the Osburn fault. Minor folding or wrinkling occurs on the limbs.

Faults cut the folded rocks in a complex manner, after causing large displacement of folded structures. The predominant east-west to northwest trend of the ore bodies is indicative of a pre-ore fracture pattern (Fig. 2).

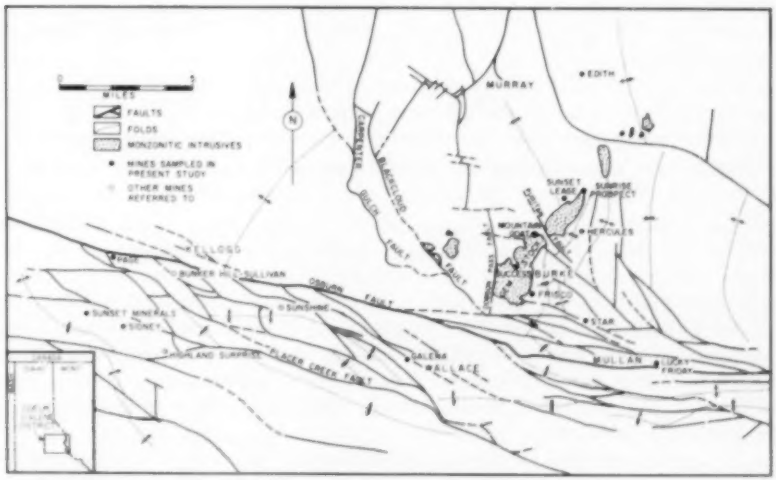

FIG. 2. Map of Coeur d'Alene District (after Whiting, 1940).

North to northwest striking thrusts and normal faults make up two groups of major post-ore faulting. All structures are apparently cut off by the last major faulting of the district, producing great east-west transverse faults, the most notable being the Osburn and Placer Creek faults.

Ore Deposits.—The base metal deposits of the district are primarily replacement veins. In addition minor fissure-filling deposits occur carrying gold, tungsten and stibnite (10). Mineralization was post-regional metamorphism.

Broadly generalized, there is a distinct horizontal distribution of the metals in a pattern of parallel to subparallel linear zones (Fig. 3). Within each zone, one type of deposit predominates. Considering the Silver Belt the center of the district both spatially and mineralogically, a typical zoned se-

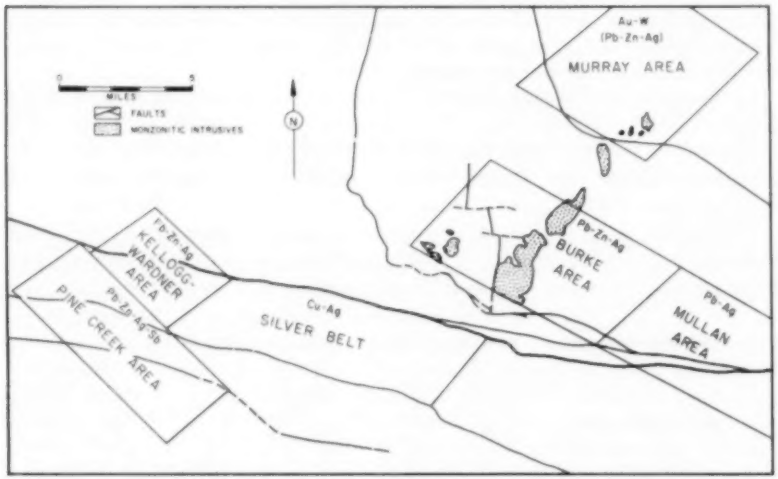

FIG. 3. Map showing metalliferous divisions of the Coeur d'Alene District.

quence of metals is present throughout the district. The rich copper-silver ores of the Silver Belt grade laterally into the zinc-lead-silver ores of the Kellogg-Wardner area on the west and the Burke area to the east. South and west from the Kellogg-Wardner area, stibnite mineralization joins the lead-zinc-silver ores of the Pine Creek area. Southeast of the Burke area the rich silver-lead ore of the Mullan area becomes the important mineralization. North of the Burke area, fissure filled gold-tungsten veins, along with minor lead-zinc-silver mineralization, bind the northern edge of the district in the Murray area.

A vertical zonation of metals within individual ore bodies is common, but not a rule. For example, the ores of the Pine Creek area, particularly the Sidney Mine, show rich lead-silver mineralization near the tops of the

ore shoots and predominantly zinc-rich ores near the bottoms (22); and iron sulfide occurs as pyrrhotite on lower levels and as pyrite in upper parts of ore shoots.

Localization of ore in the Coeur d'Alene district was dominantly controlled by structure, as ore bodies are known in all of the metasedimentary rock types and at various depths. Sulfide mineralization localized in small stringers is also known to cut intrusive stocks and associated silicic dikes.

Ore fluids gained access to now mineralized areas through parallel to subparallel closely spaced shear zones. Replacement of wall rock and minor open space filling followed the shear structures. An outstanding characteristic of the Coeur d'Alene ore bodies is the great horizontal and vertical continuity of the mineralization. Continuously mineralized strike and pitch lengths of a few thousand feet are not uncommon.

EXPERIMENTAL PROCEDURES

Galena samples were collected from mines covering the range of the mineralization types present in the district. In a few mines samples were taken through a large vertical range. Therefore, galenas of various textural types and mineral associations, various country rock associations, elevations and proximity to igneous environment are represented. The mines from which these samples were taken are shown in Figure 2.

Galena was hand-picked from ore specimens as an initial purification. About one or two milligrams of galena were dissolved in double distilled HNO_3 and taken to dryness in a 10 ml pyrex beaker. The residue was dissolved in 1 N HCl, placed on an ion exchange column (2 mm dia., 20 cm long) of Dowex-10 (200–400 mesh) and washed with 10 ml 1 N HCl. Lead then was eluted with 6 ml 7.5 N HCl and evaporated to dryness. In all cases purified reagents were used and extreme caution observed to avoid lead contamination. This procedure was found effective in separating lead ion from large quantities of iron, silver, copper, zinc, calcium and other ions which may have otherwise interfered with surface ionization of the lead in the mass spectrometer. The instrument and technique of the isotopic assay is described by Miller (16). The procedures for sulfur isotope analysis are given by Ault and Kulp (1).

RESULTS

Table 1 gives the locations and lead isotope composition of galena samples from ore structures. The lead data is given relative to $Pb^{204} = 1.000$ and by atomic per cent, with the average and the standard deviation for all fifteen samples. The uncertainty of the Pb^{204} measurement is the limiting factor in the precision of the Pb^{206}/Pb^{204}, Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} ratios. The standard deviation for the Pb^{206}/Pb^{204} ratios derived from replicate analyses on the identical sample for the present technique is $\pm 0.5\%$ of the ratio. Thus it is evident that all fifteen of the samples have the same isotopic composition within the experimental error. The S^{32}/S^{34} ratios are accurate to $\pm 0.1\%$.

SULFUR ISOTOPIC COMPOSITION OF GALENA FROM THE COEUR D'ALENE DISTRICT

Location	S^{32}/S^{34}
Sunshine Mine	
2800′ level	22.14
3840′ level	22.09

Results obtained on galena from the small sulfide veinlets in Laramide igneous rocks from the Hercules Mine, Sunrise Prospect and Success Mine are presented in Table 1.

MODEL AGES FROM LEAD ISOTOPIC COMPOSITION

As a result of the radioactive decay of uranium and thorium in the earth's crust and mantle, the isotopic composition of lead has continually changed with time. In general the ratios Pb^{206}/Pb^{204}, Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} have increased with time due to the addition of Pb^{206}, Pb^{207} and Pb^{208} to primeval lead during earth history. Thus if certain criteria are satisfied the approximate time of the formation of galena can be estimated, since the lead isotope composition remains fixed in such a mineral after formation.

The fundamental theory underlying the "common lead method" of age determination has been presented by Holmes (11), Houtermans (12), Russell and Allan (20) and Bate et al. (2). The basic assumptions in the Holmes-Houtermans treatment are: (1) the lead isotope composition of the earth was uniform at the time the earth formed and was equal to that now found in metallic meteorites, (2) small variations in the U/Pb ratio occurred due to the initial differentiation of the crust and mantle and these were preserved until ore formation, and (3) at the time of ore formation the lead was completely separated from the uranium and thus the isotopic ratio was "frozen" until the present. Another model (2) differs in the second assumption, e.g. normal lead deposits are derived from metasedimentary rocks of the crust so that all lead now in ore deposits passed through the oceans and the deposits were normally formed in a short time interval (relative to the age of the earth) after sedimentation, say 100–200 m.y. Deviations from the isotopic composition of ocean water at any given point in earth history (presumably equal to the average isotopic composition of lead in the crust) is attributed to the variation of the U/Pb ratio in the source environment and the time interval between sedimentation and the time of ore fluid formation.

The age computed from the isotopic composition of the lead in ore deposits varies somewhat depending on which model is adopted and the precise value of certain parameters, such as the age of the earth, the average U/Pb ratio in the crust or mantle, or the present average isotopic composition of the crust. These factors cause an uncertainty of about $\pm$ 200 m.y. in the time range of these deposits, i.e. 1,000–1,500 m.y.

The demonstration by Catanzaro and Gast (5) that the lead in pegmatitic feldspars yield common lead model ages in agreement with the known ages of the pegmatites by K-A, Rb-Sr and U-Pb methods strongly supports the correctness of the Bate et al (2) model and hence the validity of ore lead ages. The similarity in the isotopic composition of normal ore lead and

TABLE 1

LEAD ISOTOPIC ABUNDANCES OF GALENA SAMPLES FROM THE MAIN ORE BODIES, COEUR D'ALENE DISTRICT, IDAHO

No.	Location	204	206	207	208	207/206	208/206
1	Star Mine 850′ level	1.000 1.436	16.45 23.61	15.62 22.42	36.59 52.53	0.950	2.224
2	Star Mine 2,900′ level	1.000 1.437	16.44 23.63	15.63 22.46	36.51 52.47	.951	2.221
3	Mountain Goat Mine Ore bin	1.000 1.425	16.55 23.59	15.68 22.35	36.94 52.64	.947	2.232
4	Edith Mine, Murray Idaho (dump) (northmost in district)	1.000 1.437	16.48 23.68	15.59 22.40	36.53 52.49	.946	2.217
5	Galena Mine 3,400′ level	1.000 1.435	16.51 23.68	15.61 22.39	36.59 52.49	.945	2.216
6	Galena Mine 1,600′ level	1.000 1.435	16.38 23.51	15.60 22.39	36.70 52.67	.952	2.241
7	Page Mine 2,770′ level	1.000 1.444	16.38 23.65	15.53 22.42	36.36 52.49	.948	2.220
8	Lucky Friday Mine 1,600′ level	1.000 1.442	16.35 23.58	15.47 22.31	36.52 52.67	.946	2.234
9	Lucky Friday Mine 2,450′ level	1.000 1.440	16.44 23.67	15.58 22.43	36.44 52.46	0.948	2.217
10	Sunset Minerals 800′ level	1.000 1.440	16.45 23.69	15.56 22.41	36.42 52.46	.946	2.214
11	Sidney Mine 1,300′ level	1.000 1.439	16.43 23.64	15.58 22.42	36.48 52.50	.948	2.220
12	Sidney Mine 100′ level	1.000 1.445	16.41 23.71	15.51 22.41	36.29 52.43	.945	2.211
13	Star Mine 5,700′ level	1.000 1.432	16.46 23.57	15.60 22.34	36.76 52.65	.948	2.233
14	Sunset Lease (dump)	1.000 1.451	16.39 23.78	15.47 22.44	36.07 52.33	.944	2.201
15	Hercules Mine 1,600′ level	1.000 1.428	16.47 23.70	15.68 22.48	36.55 52.39	.949	2.211
	Average		16.44 .06	15.58 .07	36.52 .22		

pegmatitic feldspar of the same age indicates that ore lead has generally spent a relatively short time in the metasedimentary environment before being incorporated into macroscopic lead minerals.

In making the age calculations for this paper the Houtermans lead isochron diagram is used with the assumptions that the age of the earth is 4.55

TABLE 2

LEAD RATIOS FROM VEINLETS IN LARAMIDE INTRUSIVE ROCKS OF THE COEUR D'ALENE DISTRICT

No.	Location	204	206	207	208
VCF-16-58	Hercules—from east edge of Monzonite Dike	1.000	16.53	15.68	36.55
VCF-159-57	Success (Dump)	1.000	16.53	15.62	36.39
VCF-123b-57	Sunrise Prospect (Dump)	1.000	18.18	15.70	38.36

m.y., the primeval lead isotope composition was $Pb^{206}/Pb^{204} = 9.50$, $Pb^{207}/Pb^{204} = 10.36$ and $Pb^{208}/Pb^{204} = 29.49$ after Patterson (18) and average modern lead has the composition of lead in ocean water, i.e. $Pb^{206}/Pb^{204} = 18.9$, $Pb^{207}/Pb^{204} = 15.8$ and $Pb^{208}/Pb^{204} = 39.4$ (6). This is equivalent to an average U^{238}/Pb^{204} in the crust of about 9.3.

This method of age determination applies only to normal leads. Partial extraction of the more radiogenic lead from the shallow basement such as presumably formed the Mississippi Valley type deposits (7) produces leads that do not fit the model and are termed anomalous. These leads can generally be recognized by their abnormally high Pb^{206}/Pb^{204} ratios, the great variability of lead isotopic composition within the deposit and the wide variation in the isotopic composition of the sulfur isotopes.

If galena from an existing deposit is remobilized locally without appreciable contamination from rock lead in the vicinity, it will retain the original apparent age. In certain types of regional metamorphism it is possible for the galena to remain intact while the micas are recrystallized thus permitting the galena to retain a relict age.

DISCUSSION

Age of the Coeur d'Alene Mineralization.—The chronology of the metamorphic and igneous history of the Coeur d'Alene region is approximately known from reconnaissance isotopic age studies at various laboratories. Goldich (private communication) has found a K-A age of about 1,200 m.y. for phyllite of the Belt Series. This probably represents a minimum age for the initial low-grade metamorphism of this sedimentary sequence. The igneous stocks and dikes of quartz monzonite composition that are found in the district were intruded in Laramide (i.e. Late Cretaceous-Early Tertiary) time as determined by the lead-alpha method on zircons (15) and the potassium-argon method in this laboratory.

Pitchblende from the Sunshine Mine (Fig. 2) has been analyzed by Kerr and Kulp (13), Eckelmann and Kulp (8) and by Stieff (23). These results show a familiar lead loss pattern and suggest that the true age is at least 1,200 m.y. Although this clearly establishes the Precambrian age of the pitchblende, the long-standing hypothesis that the lead ores were Laramide led some geologists to propose that the pitchblende mineralization was unrelated to the lead deposition.

The isotopic analyses of the lead ores from the Coeur d'Alene District and its probable extension into British Columbia by other workers are summarized in Table 3. Most of these agree with the results obtained in this study within the experimental errors. The ratios reported by Cannon (3, 4) appear to be systematically (experimentally ?) low, but since the isochron plot is used the effect on the ages is small. The common lead ages obtained from the isochron plot using the parameters indicated above are summarized in Table 4. It is evident that all of these lead ores were probably deposited at about the same time from either the same source or similar sources and that the time of mineralization occurred about 1,400 m.y. ago. The error on the individual age estimates does not exceed $\pm$ 100 m.y. if the model is accepted as correct. The most likely error in the model would tend to make the real age even older, hence the Precambrian age for the primary mineralization of the Coeur d'Alene lead may be considered established. The only reservation to this conclusion is the possibility that the entire main body of ore represents an ancient deposit that was remobilized in Laramide time.

Isotopic Uniformity.—The samples for the present study were taken from as wide a range of geological and geochemical conditions as possible in the Coeur d'Alene district. The areal extent was 600 square miles and the vertical distribution was five thousand feet. The isotopic composition was entirely uniform over the whole district despite the variation in major mineralogical composition, i.e. lead-silver, zinc-lead, copper-silver, gold, tungsten and stibnite deposits. Thus the Murray area containing the only gold and tungsten mineralization of the district, which had long been suspected as representing another epoch of mineralization, is shown to be an integral part of the district ore, and thus merely represents a phase of the zonal sequence of mineralization in base and precious metals. Even as far away as the Sullivan Mine at Kimberley in British Columbia (Fig. 1), the apparent age is the same although the concentration of radiogenic lead may be slightly greater than in the Coeur d'Alene district. These results point to geologically contemporaneous mineralization from similar if not common sources.

The sulfur isotopic composition (Table 1) appears to be that of the average crustal sulfur (1) suggesting that the ultimate source of the ore solution may have been magmatic in nature in the deeper crust. Such an origin would permit the lead and sulfur isotopes to be an average sample of crustal material and the homogenization of these isotopes prior to injection of the ore bearing fluid.

The calculated U^{238}/Pb^{204} ratios of the environment from which this lead was produced is about 9, which is considerably closer to the U/Pb ratio in the mantle than the granitic part of the crust. This suggests that the lead that is now present in the Coeur d'Alene lead deposits spent most of its earth history in the mantle of the earth. Although it is possible that this ore fluid could have been derived directly from the mantle, based on its observed isotopic composition, it is more probable from other considerations (2, 7) that it passed through the ocean at one point in its history. If this is the case the residence time in the geosyncline prior to the formation of the Coeur d'Alene

TABLE 3

ISOTOPE ABUNDANCES OF COMMON LEAD FROM THE IDAHO-BRITISH COLUMBIA LEAD BELT

Number	Location	206/204	207/204	208/204
	Coeur d'Alene Galenas			
	This paper average of 15 samples	16.44	15.58	36.52
	Bate (2): Sunshine Mine, Kellogg, Idaho			
207	3,250-49R	16.42	15.61	36.79
210	3,700-49HWD	16.45	15.57	36.75
215 A	3,840-70S	16.52	15.56	36.85
217 A	2,800-50	16.47	15.68	36.78
170	3,700′ footwall U-vein, 60′ to Jewell Crosscut	16.89	15.47	36.87
	Average	16.55	15.58	36.81
	Cannon (3, 4)			
GS/484	Highland Surprise Mine, adit level	16.25	15.40	35.88
GS/483	Sidney Mine, slope above 500′ level	16.01	15.23	35.31
GS/482	Flathead Lake, Montana, lone crystal in calcite veinlet	16.45	15.37	35.75
GS/485	Highland Surprise Mine, 1,400′ level	16.30	15.49	36.04
GS/408	Sunshine Mine No. 2, 3,250′ level	16.01	15.12	34.93
	Average	16.20	15.32	35.58
	Farquhar and Cumming (9)			
	Bunker Hill and Sullivan Mine, Kellogg, Idaho			
	Elevations: (sea level = 0)			
	3,150 feet	16.69	15.82	36.79
	1,200	16.55	15.72	36.60
	850	16.56	15.73	36.68
	−150	16.58	15.75	36.75
	−350	16.54	15.72	36.62
	Average	16.58	15.75	36.69
	British Columbia Galenas			
	Bate (2)			
60	Sullivan Mine, Kimberly, B. C.	17.31	15.91	37.21
29	St. Eugene Mine, 200′ level, east Kootenay District, B. C.	16.41	15.59	36.59
28	St. Eugene Mine, 1,300′ level, east Kootenay District, B. C.	16.48	15.44	36.44
	Average	16.73	15.65	36.75
	Farquhar and Cumming (9)			
200	Sullivan Mine, Kimberly, B. C.	16.77	15.77	36.81
512	Sullivan Mine, Kimberly, B. C.	16.82	15.80	37.15
208	North Star Hill Mine, Cranbrook, B. C.	16.93	15.98	37.18
514	North Star Hill Mine, Cranbrook, B. C.	16.77	15.82	37.17
	Average	16.82	15.84	37.08
	Wanless (26)			
	Sullivan Mine			
	Average of 21 samples	16.66	15.59	36.39
	Standard Deviation	.09	.05	.12
	Maximum Variation	2.9%	2.7%	1.5%

leads could not have been great, or if so, the U/Pb ratio in this source area was lower than in granitic materials.

Remobilization of Ore Lead in Laramide Time.—No major ore bodies occur in the Laramide intrusives of the Coeur d'Alene district, but veinlets

TABLE 4

COMMON LEAD AGES FROM THE COEUR D'ALENE AND BRITISH COLUMBIA LEAD BELT

Deposit	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Model age
Coeur d'Alene District	16.44	15.58	1,400
This investigation (15 samples)			
Bate (2) (5 samples)	16.55	15.58	1,375
Cannon (3, 4) (5 samples)	16.20	15.32	1,300
Farquhar (9) (5 samples)	16.58	15.75	1,425
British Columbia			
Bate (2) (3 samples)	16.73	15.65	1,300
Farquhar (9) (4 samples)	16.82	15.84	1,350
Wanless (26) (21 samples)	16.66	15.59	1,300

of galena have been found in these rocks. Most geologists considered that these veinlets established the post-Laramide date of the mineralization. Thus, for example, Stringham et al. (24) say "It (i.e. the Laramide porphyritic dike in the Hercules Mine) appears at first glance to cut the mineralization suggesting 'push-apart' relationship, but small stringers of the vein minerals have been observed to penetrate the dike for a matter of inches, at several points."

Figures 4(a) and 4(b) are hand specimens and photomicrographs of sulfide (pyrite, sphalerite and galena) stringers and replacement masses in the Gem Stock monzonite from the Success Mine. The isotopic composition of this galena and similar veinlets from the Hercules Mine dike are shown in Table 2. It is evident that this galena is identical with that of the main ore and most probably represents the remobilization of some of the Precambrian ore by the Laramide intrusive.

Other veinlets (Fig. 4(c) and 4(d)) from the Sunrise Prospect Mine contain modern (i.e., Tertiary) lead indicating that the process of intrusion also mobilized small quantities of normal rock lead during the heating process. This pattern of young lead of minor quantity occurring in an area of major Precambrian mineralization has been shown in other places such as the Black Hills (14) and the Broken Hill, Australia deposits (21).

Waldschmidt (25) describes textures of galenas from the Star vein, Coeur d'Alene and concludes that long after the initial vein was formed, slight differential pressure caused the softer minerals (e.g. galena) to move by essentially plastic flow accompanied by recrystallization. Small scale lead remobilization is thus not inconsistent with some of the earlier observations. These results do emphasize the danger of inferring even relative age relations for an entire district from local and small cross-cutting sulfide veinlets associated with igneous intrusives.

It is concluded that although the deposition of the commercial ore bodies of the Coeur d'Alene occurred at about 1,400 m.y. ago in Precambrian time, local reheating occasioned by Laramide intrusives caused minor amounts of this sulfide to be remobilized. Possibly this heating also caused or enhanced the loss of lead in the pitchblende of the Sunshine Mine producing the age discordance.

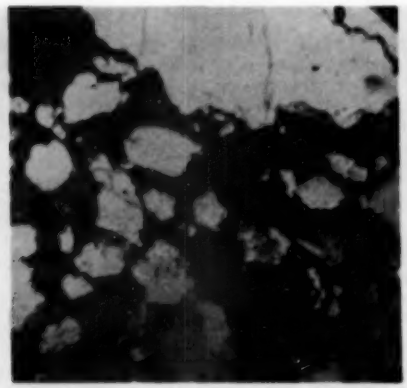

FIGURE 4a

FIGURE 4b

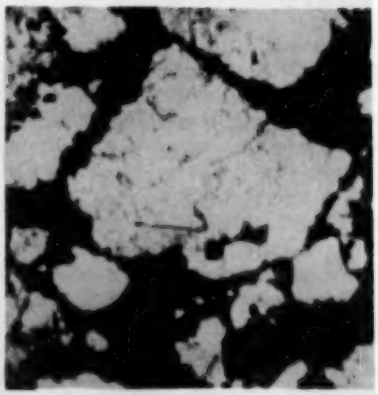

FIGURE 4c

FIG. 4a. VCF-159-57 Thin section, plain light × 82. Galena (black) replacing sphalerite (gray) and quartz monzonite feldspars (white). Galena also fills fractures in feldspar (upper right corner).

FIGURE 4b. VCF-123B-57 Hand specimen, to scale. Galena (black) stringers cutting the Gem Stock quartz monzonite from the Sunrise Prospect Mine.

FIG. 4c. VCF-123b-57 Thin section, plain light × 82. Galena (black) fracture filling and replacement of quartz monzonite feldspars (white).

If limited remobilization of lead ores is demonstrated in this situation it might be expected that under certain conditions of more widespread and sustained heating, large quantities of older primary lead ore might be redeposited without significant contamination by contemporary rock lead.

Such an occurrence appears to have been found in the Urals by A. P. Tugarinov (private communication). This process may present some ambiguity in the interpretation of lead isotope data alone. Nevertheless, if the absolute age of mineralization may be determined independently and the geological relations are clearly understood, these data provide a powerful insight into the mechanism and origin of ore deposition in a given locality.

CONCLUSIONS

1. Near conformity of Beltian sediments with overlying Cambrian in Montana had led stratigraphers to place the Belt Series in late Precambrian. The recent isotopic studies, however, necessitate moving Beltian age back into Archean time with a minimum age of 1,400 m.y.

2. Uranium and primary lead mineralization was essentially contemporaneous, occurring about 1,400 m.y. ago.

3. The lead isotopic ratios indicate derivation from a single, homogeneous source during one mineralizing epoch, this source having a U/Pb ratio similar to basalt. This does not preclude residence of the lead for a short time in an environment of higher U/Pb ratio prior to ore formation.

4. Local remobilization of ore and rock sulfide occurred during Laramide disturbance as a result of igneous intrusions.

These results suggest that spatial relationships between ores and intrusives do not necessarily imply genetic relationships. There appears to be an immediate necessity for re-examining the interpreted Laramian age of deposits in Precambrian rocks along the Laramide orogenic trend. The possibility that large scale remobilization of an ore deposit exists.

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GEOCHEMICAL LABORATORY, LAMONT OBSERVATORY,
COLUMBIA UNIVERSITY, NEW YORK,
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ON THE BLIND RIVER URANIUM ORES AND THEIR ORIGIN

D. S. ROBERTSON AND N. C. STEENLAND

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ABSTRACT

Ore conglomerates of the Blind River area lie at or near the base of the Huronian sedimentary section in discontinuous, sheet-like, partly overlapping, south east trending zones within a major north northeast belt. They are part of a sequence of detrital sediments laid down in a beach and delta environment by a northward transgressing sea.

The Huronian rocks are cut by basic dikes and by quartz veins, both of

which have been dated. The ore conglomerates are older than 1,200 M.Y. and probably older than 1,700 M.Y.

The uranium minerals, brannerite, uraninite and a "monazite" complex, occur with a typical detrital assemblage and appear themselves to be detrital.

The ore minerals are considered to be syngenetic and of the age of the conglomerates. Age determinations on the ores suggest that the radioactive minerals have been modified, or that material has been introduced, at 1,300 M.Y. and at 600 M.Y.

Differences between the Witwatersrand and Blind River are discussed briefly.

INTRODUCTION

THE Blind River area has leaped into prominence in the last five years because of its tremendous impact on the world's uranium reserves. It has reached similar geological prominence partly because of its inherent importance as a mineral producing area, but more largely because of its similarity to the Witwatersrand and its gold-uranium ores, the origin of which has provided much argument and little agreement for many years.

Over 800,000 feet of diamond drilling have provided considerable data on the ore bodies, their relation to each other and to the surrounding rocks. All of the operating mines, at the time of writing, have been producing ore for at least one and one-half years. Considerable data has accumulated from underground studies.

The purpose of this contribution is to present some of the results of the authors' studies, which have covered many of the operating mines, representative drill data from all of the area and many phases of the geology of the broader region, and to relate them to data provided by other workers in the field.

GENERAL GEOLOGY

The rocks of the Blind River area are part of an assemblage that stretches in an elongate belt for over two hundred miles, lying both to the east and west of Blind River. The structural modifications, the character of late metamorphism and late hydrothermal activity, the last characterized by widespread fracture fillings of various sulfides, are all characteristic of this belt. Studies of Blind River geology require not only study of the details of its ore bodies and surrounding rocks, but also study of data from the Sudbury area and the area northwest of Sault Ste. Marie.

The basement rocks over the larger area are composed of metamorphosed volcanic rocks and sediments with acid and basic intrusives of varying ages. Over the basement, commonly considered as of Archean age, lie the Huronian sediments. The uranium deposits of the area are associated with the lower part of the Bruce series lying immediately above, or close to, the profound unconformity between "Archean" and Huronian.

The rocks along the north shore of Lake Huron, which area includes the Blind River area, were mapped by Collins (4). His studies have proven to be remarkably accurate and more recent work has largely provided more

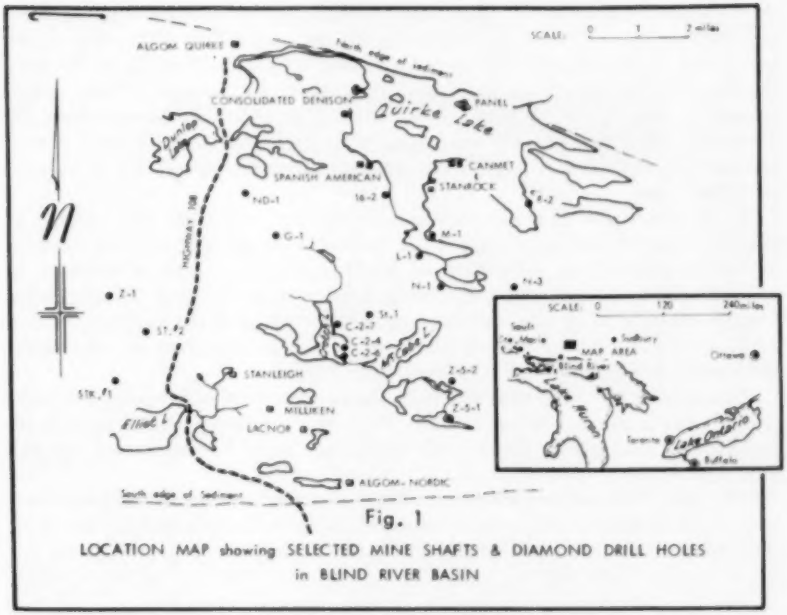

Fig. 1

LOCATION MAP showing SELECTED MINE SHAFTS & DIAMOND DRILL HOLES in BLIND RIVER BASIN

FIG. 1. Map of the Blind River basin showing selected shafts and diamond drill holes used in diagrams or referred to in the text.

detail with respect to stratigraphic variation and rock distribution. Roscoe (28) has provided the most recent stratigraphic column reproduced as part of Table 1 and he summarizes known data on rock distribution in a map appended to his report.

Over the larger area the Huronian rocks are metamorphosed, folded, faulted and soaked with late sulfide. Metamorphism is regionally of low grade (greenschist facies) upon which is superimposed the effects of a multitude of basic intrusives, which locally produce meta-hornblende-rich rocks, and physical effects resulting from major faulting. Physical effects appear to become intensified from north to south, culminating along the north shore of Lake Huron at the Murray series of faults and along the Keewatin-Grenville boundary south and east of Sudbury. Physical effects along faults in the mines of the Blind River area vary from the complete absence of crushing, even in the face of factual evidence of movement, to the production of a few inches of mylonite or a few feet of general coarse crushing. Faults appear to be largely of one general age, that associated with production of the major thrusts. As the major faults appear to be associated with faults cutting the Sudbury basin, the faults are younger than, or about the same age, as the Sudbury rocks.

Superimposed on earlier phenomena is what may be called a regional soaking with sulfide. Pyrrhotite, chalcopyrite and sphalerite with some pyrite and galena occupy joints, fractures, faults and shears in all of the rocks from the basement to the youngest Huronian observed. The zone of the sulfide soaking appears to be narrower than the zone in which Huronian rocks are developed, lying more closely associated with the north shore of Lake Huron and curving northeast through Timagami on the north side of the Keewatin-Grenville edge.

It is conceivable that the sulfide soaking is a late stage of a period of orogeny, the beginnings of which are indicated in the Blind River area by the early geosynclinal deposition of Early Huronian sediment followed in order by basin development and folding, faulting and intrusion of basic rocks. Locally faulting post-dates sulfide and basic rock and the authors do not imply a sharp cut-off to any one phenomenon, rather a process in which some phenomena are generally of later time than others.

Latest activity in the area has been the emplacement of large quartz-veins or dikes, in places over 20 feet in width, with which volumes of chalcopyrite are occasionally associated. Some basic dikes may be of Keeweenawan age and thus very young.

The lower Huronian rocks in the Blind River area lie in a broad east-west trending anticlinal and synclinal structure, with the south limb of the anticline lying in the foot wall of the east-west striking Murray fault along the north edge of Lake Huron. Erosion has removed the core of the anticline so that the contact of the sediments forms a large Z in outline.

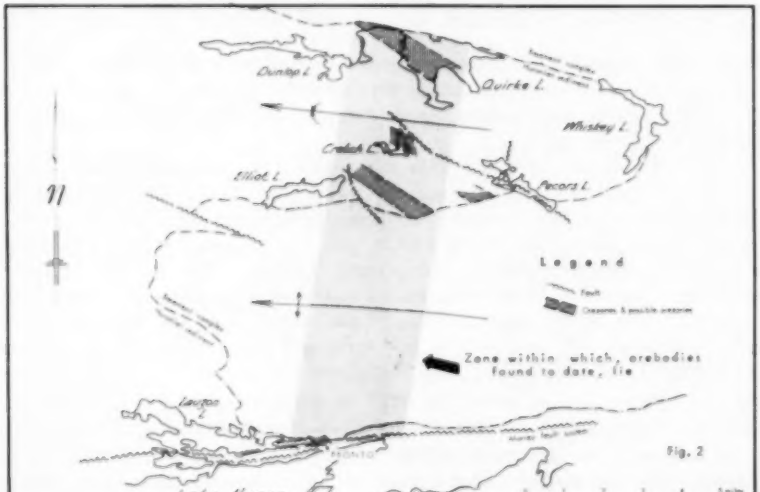

FIG. 2. Map of the Blind River area showing ore zones and major fault zones.

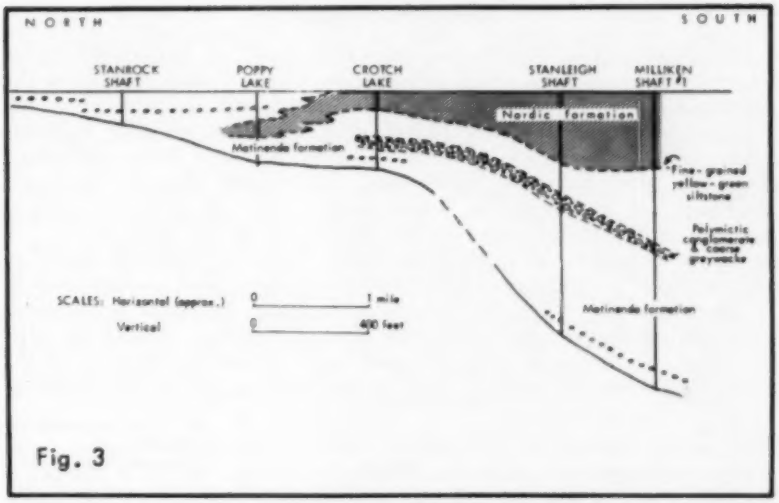

FIG. 3. Section across the basin using the base of the Middle Mississagi as a horizontal datum. The place of the Nordic formation in the Poppy Lake holes is indefinite but is drawn to illustrate the concept of transgression and regression. As shown at the north end of the section, the ore conglomerates may overlap. The authors believe, for example, that the Algom Quirke ore conglomerate zone is stratigraphically higher and overlaps the Consolidated Denison ore zone. Similarly, the Consolidated Denison ore conglomerate zone may overlap the Stanrock-Spanish American zone.

The Pronto deposit described in some detail by Holmes (14) lies in the south limb of the anticline. The remaining producing deposits occur on the north and south edges of the syncline. A new mineralized conglomerate zone has been indicated by drilling toward the basin center (Fig. 2).

There is evidence (Fig. 3) that the ore zones have a transgressive relationship to a south sloping basement and that the zones are both higher in the geological section and younger in age from south to north. It has been established that there is no lateral connection between the Quirke Lake ores and those to the south, and that there is no connection between the Crotch Lake zone and zones to either side.

STRATIGRAPHY

The stratigraphic section as described by Collins (4) has recently been expanded in some detail by Roscoe (28). Frarey (10) has studied the section to the west and data on the rocks to the east have been provided by Thomson (33). The section is particularly well described by Roscoe (28) and in the volume prepared for the Sixth Commonwealth Mining and Metallurgical Congress (37). This paper will discuss only the Mississagi section, except where reference to higher units has significance.

Mississagi Formation

The Mississagi is divisible into three units based on distinct differences between the sediments of which they are composed. Collins referred to the southward thickening of the Mississagi as a whole and placed its maximum thickness between 10,000 and 12,000 feet. Maximum probable thickness on the south limb of the syncline as projected from drill holes and surface exposures, is approximately 4,000 feet. The thickest part of the Upper Mississagi seen by the writers is towards the centre of the basin. This is also true of the thicker parts of the Middle Mississagi (Figs. 6, 7). A general thickening to the south of the Lower Mississagi seems probable but a thickening of the Middle and Upper formations has at least not been proved.

The terminology of Collins' original Mississagi formation is becoming somewhat jumbled with the introduction of Roscoe's terms. Use of the term, Mississagi, by Roscoe as a Group name seems unfortunate because of the broad popular use of the term, both in the literature and by the geological

Nomenclature of Collins		Nomenclature of Roscoe		Common Terminology	
Formation	Series	Group	Formation		
Lorraine	Cobalt			Lorraine	Upper Huronian
Gowganda		Dunlop	Gowganda	Gowganda	
Serpent	Bruce	Quirke	Serpent	Serpent quartzite	Middle Huronian
Espanola			Espanola	Espanola limestone	
				Espanola greywacke	
				Bruce limestone	
Bruce			Bruce	Bruce conglomerate	
Mississagi		Mississagi	Ten Mile	Upper Mississagi	Lower Huronian
			Whiskey	Middle Mississagi	
		Elliot	Nordic	Lower Mississagi	
			Matinenda		

TABLE 1

Stratigraphic sequence
showing relation of varied terminology

fraternity in general. Although the writers agree with Roscoe's concepts, the common terminology indicated in Table 1 will be used throughout this paper and Roscoe's terms will be introduced only where clarification is needed.

Lower Mississagi.—The Lower Mississagi section thickens from zero feet at Quirke Lake, where it is locally overlapped by the Middle Mississagi, to approximately 700 feet north of the Algom-Nordic mine. Thickening is not continuous, a shelf-like area underlies the present centre of the basin (Fig. 3). Local variation in thickness is pronounced, being at least partly caused by topographic highs and lows in the basement rocks. It has been suggested that greenstone basement zones form depressions relative to granite or gneiss basement and that these depressions control the place of ore deposition. That basement depressions partly control the place of ore deposition is seemingly true as is well illustrated by Roscoe (28). However, the relationship between granite and topographic culminations is not proved. Most basement highs known to the authors are composed of greenstone. They are in places of such magnitude that prevented deposition of any of the Matinenda formation, in which ore might normally exist. On the northern edge of the syncline, for example, ore is not continuous between Can-Met and Stanrock because of a northwest trending greenstone high that cuts out some 100 feet of section between the properties. Locally, the Matinenda is not present at all, the basal conglomerate of the Middle Mississagi lying directly on the basement.

In the center of the basin and further south, on the south limb of the anticline, various marker horizons permit one to follow basement highs with ease. Figure 5 shows one such greenstone high north of Elliot Lake. The trend of this high seems to be northeasterly. Further east a greenstone high is encountered south of Flying Goose Lake.

On the south limb of the syncline, the Lower Mississagi can be divided into a number of units. The principal markers or recognizable individuals are shown in Figure 3. The interbedded argillite and graywacke above the fine grained yellow argillite is approximately equivalent to Roscoe's Nordic formation.

As indicated by Roscoe, the Nordic formation is restricted to the southern part of the syncline but Nordic-like rocks have been noted in the Nasco No. 1 drill hole south of the west arm of Quirke Lake. The formation consists of interbedded argillite, siltstone and graywacke, the argillites normally being more plentiful at the upper part of the section and the graywacke being more common towards the bottom. Over most of the area in which the Nordic formation is developed, the lowest argillite is a fine grained yellow to yellow-green unit varying between 6 and 12 feet thick. One would anticipate that, due to its constant character and its widespread distribution (Stanleigh, Milliken, Lacnor, Crotch Lake) at an apparently constant stratigraphic position, it was deposited during a period of quiescence and would be a good stratigraphic marker. It has been used as such in studying some of the details of drilling in the south range. It is suggested that the lower contact of the Nordic formation be redefined as the base of this marker horizon rather

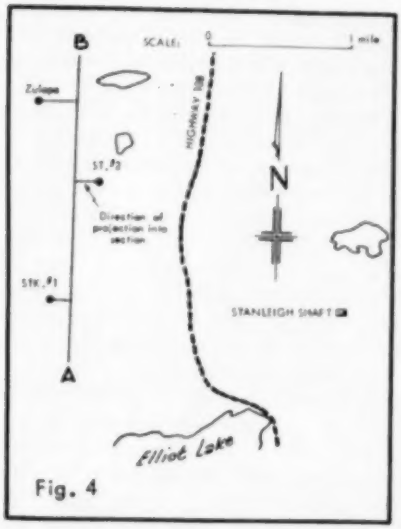

Fig. 4

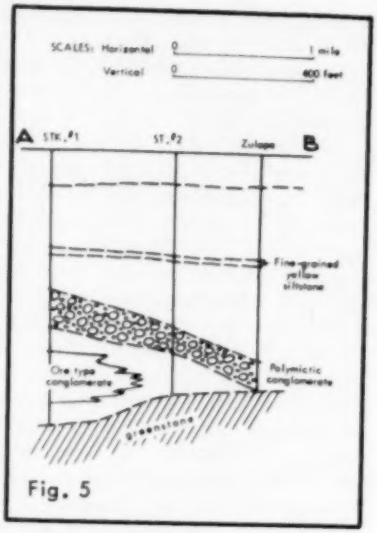

Fig. 5

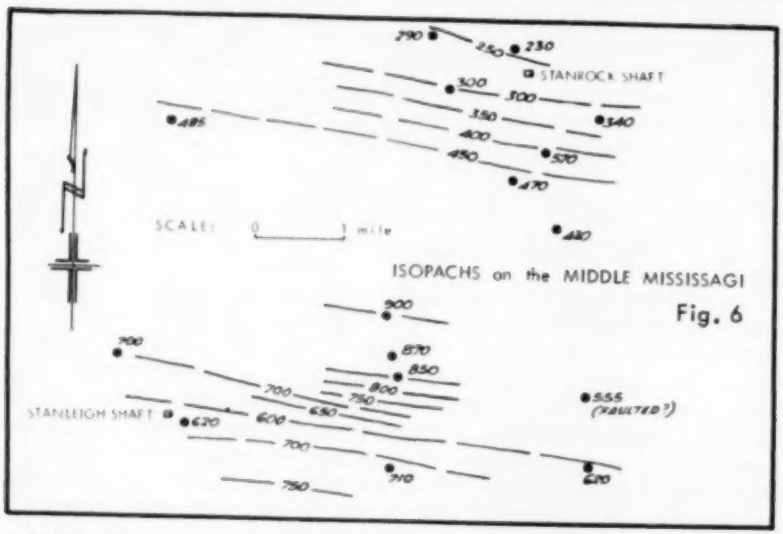

FIG. 4. Plan of area north of Elliot Lake relating drill holes of the section of Figure 5.

FIG. 5. Section through area shown in Figure 4. The approximate attitudes of the fine grained yellow siltstone and the base of the Middle Mississagi are taken as the horizontal with the siltstone taken as a datum plane. The basement high and the cross cutting character of the polymictic conglomerate are shown. It

than in an indefinite way as an arbitrary horizon ". . . above which graywacke beds are thicker than the intervening quartzite layers" (28, p. 8).

The Matinenda formation comprises the lower part of the Lower Mississagi on the south limb of the syncline and the full Lower Mississagi section on the north limb. It is composed of medium to coarse grained clastic rocks varying from grits to oligomictic quartz pebble conglomerates and polymictic conglomerates, all carrying abundant feldspar. Bedding is poor and cross bedding is common. Scour channels are observed particularly in the mines where excellent conglomerate sections are cut partially away by scour channels filled with barren arkose.

The quartz pebble ore conglomerates are normally at the base or within 150 feet of the bottom of the section. Wherever ore-type conglomerate is found, the surrounding rocks are found to be largely medium to coarse grained, yellow arkose, the yellow color being derived from abundant yellow sericite. This sericite appears to be due to feldspar breakdown and alteration of clays. These arkoses commonly occur above, within, below, and laterally off the edges of the ore conglomerate as if they form an envelope within which ore conglomerate lies. This connection is so marked that it can be used as a prospecting tool in the search for conglomerate, the arkose envelope forming a larger target than the conglomerate beds.

Discontinuity within the Lower Mississagi section is suggested at a number of places. The most pronounced is in the area of the south limb of the anticline where a polymictic conglomerate, Figure 5, is at least locally cross cutting.

This polymictic conglomerate is composed of poorly sorted quartz pebbles and fragments from pea-size to cobbles. Greenstone and argillite-like fragments occur throughout the unit, giving it a distinctive appearance. Pyrite is common. Packing varies considerably and in some cases there is little in the way of interstitial material, although elsewhere an argillaceous matrix is common. Locally it is highly radioactive.

The conglomerate has the aspect of local origin. Conceivably ore-bearing conglomerate has been exposed during development of this unit, erosion of the former providing radioactive material for the latter. In Diamond Drill Hole C-2-7 on Crotch Lake, the polymictic conglomerate impinges on ore-type conglomerate.

Middle Mississagi.—The Middle Mississagi thickens from about 200 feet in the Quirke Lake vicinity to about 900 feet in the Crotch Lake area. South of Crotch Lake it thins to approximately 700 feet through the Milliken property.

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seems obvious that something other than the position of the basement high, at this locale, affects the development of the ore conglomerate.

FIG. 6. Isopachs of the Middle Mississagi showing thickening of the sediment in the center of the basin at this early stage. The isopachs are constructed with data derived from drill holes and corrected for hole deviation from the vertical. Corrections for observed faults have been made where possible. Where faulting is observed or suspected and no correction is made, the word (faulted?) appears on the plan.

A distinctive polymictic conglomerate commonly known as "the argillite conglomerate" forms the basal member of the unit. Carrying pebbles and boulders of quartz, granite, greenstone, and metasediment in a matrix varying from argillite to graywacke, it is pyrite-bearing and slightly radioactive.

This member cuts out the ore conglomerate on the east and west edges of the Algom-Quirke property in erosional fashion (13). Radioactive material contained therein possibly is derived from Lower Mississagi ore conglomerates that have been eroded. The widespread radioactivity in this conglomerate may indicate that Lower Mississagi ore conglomerate occurred considerably farther north prior to Middle Mississagi time and that there is a considerable erosional interval between Lower and Middle Mississagi deposition.

The upper parts, and the bulk of the Middle Mississagi consist of interbedded layers of argillite, siltstone, and graywacke. The beds show pronounced grain gradation grading from argillite down to graywacke on a fine scale.

Upper Mississagi.—The Upper Mississagi thickens from about 900 feet in the Quirke Lake area to about 1700 feet north of Crotch Lake. It then thins somewhat through Stanleigh and Milliken, being about 1500 feet thick in each of the Stanleigh shafts.

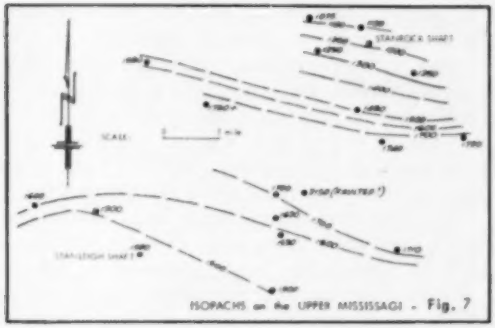
The rocks are mainly arkoses and graywackes, which are heavily cross bedded.

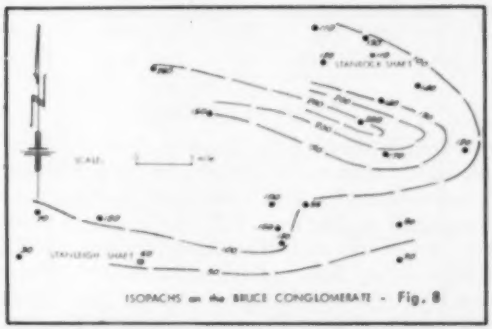
Origin of the Mississagi

Studies of pebble orientation and cross bedding suggest that the Lower and Upper Mississagi materials were deposited in a direction southwest to south parallel to the long axes of the ore zones and to the long axes of at least some of the basement topographic features. It has been suggested that pre-Huronian relief strongly influenced early deposition and that the place of ore zones is governed by the presence of topographic lows controlling the sources of paleostreams.

In general, the Mississagi section is similar to the gross section in the Gulf Coast area attributed by Van Siclen (34) to a cyclic transgressing sea. Terrigenous, shallow water sediments at the base are overlain by deep water facies in the middle and overlain by shallow water facies at the top. A similar manner of origin for the Mississagi was suggested by the authors in 1956 (27). Relative to the Lower Mississagi, it was stated that ". . . the conglomeratic sediment . . . is a product of cyclical fluctuation of the land mass during a general lowering of the base level which caused periodic deposition of conglomerate into a trangessive sea in Lower Huronian time."

Isopachs of the Middle and Upper Mississagi, (Figs. 6 and 7) indicate that the Blind River basin began its development in Middle Mississagi time with the thickening of sediment towards its center.





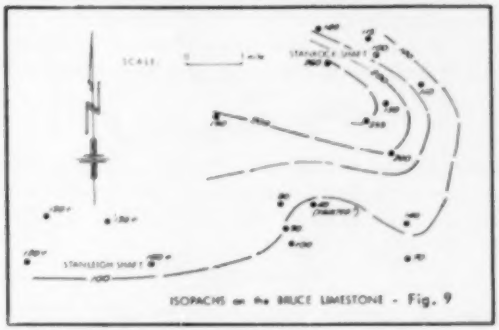


FIG. 7. Isopachs of the Upper Mississagi.
FIG. 8. Isopachs of the Bruce Conglomerate showing pronounced basin development.
FIG. 9. Isopachs of the Bruce Limestone showing pronounced Basin development.

STRUCTURE

Two major structures occur in the area, the basin or syncline itself and the strong faults along the north shore of Lake Huron, which have been related to the Murray fault system that cuts the Sudbury basin.

As has been shown earlier, the syncline developed slowly through a long period of time, equivalent to the deposition of some 5,000 feet of section at its thickest part. The area was base levelled and the Gowganda rocks of Cobalt time and the Lorraine arkoses and quartzites were spread over a large area. Intense faulting then took place along the present north edge of Lake Huron and at least one large-scale thrust fault developed in the basin. Following this, many high-angle faults, some of large displacement, developed.

The Murray fault system has been described by Abrahams (1) and Holmes (14). Suffice it to say that movement along its many individuals is in terms of thousands of feet, the Pronto ore body being cut off against one of the faults that thrusts granite over the sediments to the north for a displacement of over 1,000 feet. Collins (4) places the vertical movement on the Murray Fault at 6,500 feet.

Thrusts in the Basin

One major low-angle thrust fault has been discovered in the basin that cuts the ore on the Northspan (Spanish American)-Stanrock properties. This fault varies considerably in both strike and dip, its attitude being almost of bedding plane nature at Stanrock (10°–15°) and of much higher angle (30° plus) where it surfaces at Consolidated Denison. Net slip, calculated on the basis of offset on the Stanrock ore body, is over 1,200 feet in a northeasterly direction. Vertical displacement of ore ranges from about 10 feet north of the Stanrock No. 2 shaft to approximately 100 feet at the Stanrock-Spanish American boundary.

Small thrusts at low angle have been observed elsewhere in the basin. Those on the south limb dip to the north, and those on the north limb dip to the south.

Reverse Faults

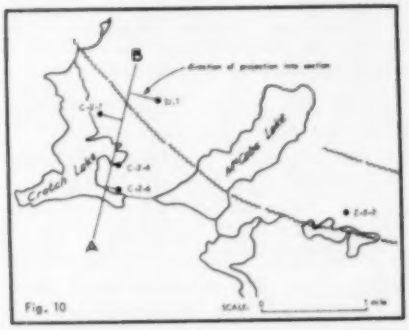
Reverse faults are not uncommon in the area. The majority of the faults at Stanrock, on top of the thrust sheet, are of this type as are those at Stanleigh and Milliken. Vertical offset varies from 1 foot to 12 feet on the Stanrock property.

Normal Faults

Normal faults are common throughout the area. Vertical displacement of as much as 400 feet has been noted on a north-south striking normal fault along the west edge of the Stanleigh property, and vertical displacement of over 150 feet has been postulated on a northwesterly striking normal fault north of Flying Goose Lake. This latter fault continues to the west and is shown on Figure 11 where the vertical displacement is over 400 feet. A normal fault of considerable magnitude occurs near the east end of Matinenda Lake. It also trends northwest.

General

The regional fault pattern consists of three main directions of faulting in which the above described types lie, a northwest system, a north to northeast system and an eastwest system. The low angle thrusts of the area, as far as is known, have eastwest strikes. Major high-angle movement seems confined to northsouth faults, or northwest trending faults. It is of interest that faults in opposite blocks of the major Quirke Lake thrust appear to have different types of movement. Faults subsidiary to the thrust in its upper block themselves exhibit a manner of yielding characteristic of continual compression, while the subsidiary faults in the lower block develop in fashion suggestive of relaxation and tension. In connection with this, it is of interest that at both Can-Met and Consolidated Denison, in blocks adjacent to and close below the major thrust, volumes of basic rock have been observed



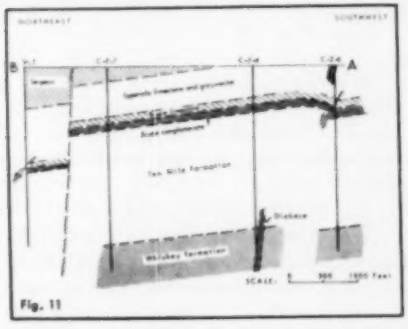


FIG. 10. Plan of area in Crotch Lake vicinity relating diamond drill holes of Figure 11 and showing part of major fault.
FIG. 11. Section to accompany Figure 10 illustrating faults in the basin.

Trend	Can-Met (below thrust)	Stanrock (above thrust)
N. W.	N. dip normal	S. dip reverse
E. W.	S. dip normal	N. dip reverse
N. S.	E. dip normal	

that entered and percolated through the ore zones—conceivably because of tensional openings that facilitated their ingress. Such phenomena have not yet been observed at Stanrock or at Spanish American immediately above the major thrust.

The faults are not normally mineralized and in particular they show no signs of radioactivity, even in the immediate vicinity of the ore beds.

ECONOMIC GEOLOGY

Descriptions of the area give the heavy minerals found in and adjacent to the ore bodies all with the same emphasis without discriminating between them on the basis of character of occurrence or time of origin. In a recent contribution, Davidson states (*7*, p. *672*):

> At Blind River not only are cobalt and copper sulphides and arsenides present in small amounts in the reefs, but transgressive shear vein deposits in the same district, at Pater Uranium Mines, are mineralized with these metals to a workable extent. Since cobalt is the most common companion of uranium in undoubted hydrothermal associations, the coexistence of the two elements in the bankets is another strong argument against a syngenetic origin.

This argument ignores certain facts. Chalcopyrite in the ore bodies occurs only in late cracks with pyrrhotite and other sulfides. All of these are more common elsewhere in the section, in the Middle Mississagi argillites or in the Bruce limestone for example, than they are in the ore conglomerates. Cobaltite is extremely rare. Most authors who have studied polished sections or heavy mineral suites from the conglomerates do not mention its presence. It also involves the Pater Mine, a deposit of completely different character and probably of different age. The extremes to which supposed geochemical relationships can be pushed cou'd not be better illustrated.

The heavy minerals in the conglomerate bodies belong normally to one of two classes: 1) those that are of obviously detrital character including monazite, uraninite, brannerite, zircon, diopside, etc., and 2) those that are obviously of late, crosscutting character, being invariably associated with fractures or quartz veins. These include chalcopyrite, pyrrhotite, sphalerite, pitchblende, thucolite, and large size galena crystals. There is one mineral that is not definitely of either character and has two modes of occurrence, and this is pyrite.

For convenience, the mineralization in the area can be classified into two types, a) the Blind River type of uranium-bearing conglomerate, which is the only type of economic importance in the area at the moment, and b) the other mineral occurrences. We will discuss the latter group first.

Mineral Occurrences Other Than the Blind River Type

Mineral occurrences in the area have been described by Knight in 1915 (16), and by Moore in 1929 (20), as well as by many other authors. A recent description of one deposit has been published by Freidman (11).

Pyrrhotite-Chalcopyrite Deposits.—Gabbroic, dioritic and diabasic rocks commonly display rusty surfaces caused by oxidation of the sulfides, pyrrho-

tite and chalcopyrite, which occur in spots disseminated through the rock and in thin films on fracture surfaces. Moore describes a nickel-copper deposit (20, p. 25) that "resembles some of the spotted norite from the Creighton mine. . . ." The surface gossan "is about 2100 feet long with a maximum width of 200 feet. The pyrrhotite and chalcopyrite are quite uniformly distributed through the country rock in blebs and the chalcopyrite also forms films along the joints. . . ." This type of occurrence, on a smaller scale, is common throughout the district between Sudbury and Sault Ste. Marie and east of Sudbury.

Chalcopyrite-Pitchblende Occurrences.—At Cobre Lake, northwest of Quirke Lake, in the southwest corner of Township 1A, a large diabase, body develops associated granophyric masses and veinlets carrying disseminated chalcopyrite and minor amounts of uranium in the form of pitchblende. This dike cuts the Gowganda arkose and conglomerate and the mineralization is thus definitely later than the host rock of the Blind River mineralization. The quartzite, arkose and conglomerate in the vicinity is radioactive due to widespread monazite but the mineralization in the diabase does not affect the sediments. A similar occurrence is described at Theano Point (22) where pitchblende without chalcopyrite occurs associated with diabase.

Copper Mineralization in Shear Zones.—At Spragge, Ontario, Pater Mines has disclosed a copper-cobalt deposit to a depth of several hundreds of feet, and with considerable lateral development. This occurrence associated with a shear in the basement appears to be a culmination in the regional soaking attendant on, or after, the intrusions of Sudbury type. Similar occurrences, of smaller size, are numerous both east and west of Blind River.

Chalcopyrite in Quartz Veins.—Cutting the Gowganda and Lorraine rocks along the White River road, west of Blind River, are many large quartz veins with which are associated masses, blebs and specks of chalcopyrite in bands 6 to 10 inches wide exposed in several places.

Other deposits of the same character are known, the principal one being the Bruce Mines Copper deposit originally discovered in 1846, described by Knight (16, p. 231). Moore's summary is of interest (20, p. 10):

> This deposit is of much interest to the geologist and prospector because it is a type more or less characteristic of this region. The occurrence of chalcopyrite carrying traces of gold in quartz veins with barite and calcite is duplicated on other properties. The veins are of the fissure type with little replacement of the wall rock, and like the others in this area, they are associated with the Nipissing diabase. They are later than the diabase itself, but they have resulted from movements that apparently occurred when adjustments in the earth's crust followed the intrusion of great quantities of diabase. The solutions forming the veins escaped at depth from the underlying magma from which the diabase rose at an earlier stage of the igneous activity. There was not enough differentiation in situ in the diabase itself to produce the ore as there was in the Sudbury nickel eruption. . . .

Cobalt in Acid Phases of Diabase.—Cobaltite has been found at a number of occurrences in acid segregations on the edges of diabase bodies or associated with pegmatoid pods of quartz and feldspar. An exposure visited by

the writers on the Spanish River just west of Espanola contains cobaltite crystals one-half inch on edge. A similar occurrence is described by F. F. Osborne (23, p. 65).

Pyrite-Bearing Meta Sediments.—On Flack Lake, northwest of Quirke Lake is a pyrite deposit recently described by Freidman (11). He suggests that the deposit belongs to the "submarine exhalative sedimentary ore body type" in which underwater volcanic activity produced volumes of H_2S that permeated clastic sediments transforming magnetite and iron hydroxide gel contained therein to pyrite. Traces of cobalt, silver and gold are reported.

Thorium-Rich Sediments.—Thorium-rich sediments of Cobalt age are found at numerous localities. The Cobalt sequence is radioactive at many stratigraphic levels, the radioactivity being due to monazite in every case investigated by the authors. A 1,300-foot drill hole put down in Township 1A, just west of the Cobre Lake copper and copper-uranium showings cut material showing radioactivity wherever thin pebble bands were intersected. These same Cobalt rocks are radioactive north of Quirke Lake in Township U and north of Sudbury in Roberts and Creelman Townships.

The thorium-rich sediments described by Vickers (35) and which Davidson implies are of the same age as the Blind River conglomerates, are of Cobalt age and comparable to the Cobalt sequence described above, not to the Mississagi.

In General

None of the deposits described above are radioactive except the monazite-rich sediments of Cobalt age and the Cu-U mineralization with chalcopyrite and pitchblende associated with diabase.

Many of the diabases described by early workers as Nipissing or Keweenawan are considered by the authors to be akin to the basic rocks associated with the Sudbury eruptive, particularly to the gabbro, quartz diorite and diabase so well developed below the base of the eruptive in Trill Township on the west end of the Sudbury Basin. The Sudbury deposits "have been well dated at about 1200 M.Y. . . ." (5, p. 45). The basic rocks of Trill Township contain typical Sudbury-type mineralization and appear to be of similar age.

The mineralization at Theano Point (22) is similar to that at Cobre Lake and is associated with Keweenawan-type diabase. Pitchblende from these deposits is well dated, again in the neighborhood of 1200 M.Y. (5, p. 45). Cummings, Wilson, et al. (5) state that, "this suggests that the very late Precambrian age often assigned in the past to such dikes (Keweenawan type) is not in all cases justified." The authors believe that there is more than one type and age of dike or basic rock, but that base-metal mineralization is associated primarily with those of one age.

Wherever basic rocks of the kind described occur, and they are widespread, chalcopyrite and pyrrhotite segregations and fracture fillings are found. Radioactivity is not associated with them except in the few cases such as Cobre Lake where pitchblende and chalcopyrite are intimately associated, and Theano Point. Metamorphosed basement rocks commonly con-

tain sulfide filling fractures and shears along the length of the north shore of Lake Huron and northeast through Timagami. As these sulfides and the basic rocks have a similar area of distribution there is believed to be a connection between them and their age is considered to be about 1,200 M.Y. These sulfides have the same general composition, appearance and manner of occurrence as those found throughout the Bruce series in the Blind River area. Figure 17 illustrates chalcopyrite and pyrrhotite (black) in fine fractures approximately normal to the bedding in the argillite or Middle Mississagi. The sulfide is concentrated in the coarse grained bands presumably because of their relative brittleness and the open character of the fractures where they cut the brittle bands.

A quartz vein cutting a large diabase body and carrying pyrrhotite, chalcopyrite and galena is described by Moore (20, p. 15). The diabase cuts the Gowganda rocks in the area. A specimen of galena from this vein yields an age of 1,310 M.Y. plus or minus 180 M.Y. (5). The quartz veins are thus shown to have an age similar to that of the diabase dikes.

Quartz veins cut the Stanrock ore body and carry chalcopyrite, pyrrhotite, and in places galena and sphalerite. They are typical representatives of the group described earlier. They cut across fault zones underground and are thus very late in the sequence. Moore (20) considers them later than the diabase. They have no observable connection with the radioactive mineralization, and, as elsewhere, they are not themselves radioactive.

Basic dikes, lamprophyres, diabases, and chlorite-rich rocks cross many of the properties. They are not radioactive. At Can-Met and at Consolidated Denison the chlorite-rich dikes permeate the ore-bearing conglomerate causing development of chlorite and hornblende in the sediment and replacing even the quartz pebbles to the point where bands of pyrite grains, largely untouched, traverse a rock, largely chlorite in composition, and maintain the original banded appearance.

The study of many of the above described deposits and consideration of both their regional aspects and their probable relationship to features seen in drill core and in underground workings in the Blind River area, suggest the following to the authors:

1) that the common sulfides in the Blind River ores (except pyrite) are regional phenomena in no way related to the conglomerate or to the uranium content thereof,
2) that their age is about 1,200 M.Y. as is that of the quartz veins and many of the basic rocks with which the broader area abounds. The age of the uranium mineralization must be older than this.

The Uranium Bearing Conglomerates

The ore-bearing conglomerates are quartz-pebble conglomerates with pebbles varying in size from about ¼-inch to 2 inches. Locally larger pebbles occur and boulders up to 2 feet in size have been described from the Pronto deposits where the conglomerates are basal (14). As the conglomerate beds thicken and thin, pebble size varies considerably. In general there appears

to be a coarsening in size of pebbles from north to south, i.e., from Quirke Lake to Pronto.

White quartz pebbles predominate but gray quartz is common, possibly due to radioactive bombardment of the quartz. Black chert pebbles and a few pebbles of jasper are found. Rare granite pebbles have been reported and rare yellow arkose pebbles, composed of material similar in appearance to the arkose envelope, are found.

The pebbles are normally well rounded. However, in the Stanleigh-Milliken-Lacnor area, elongate, shard-like pebbles and fragments of a creamy-gray or brown colored rock of very fine grain are found. These normally occur in volume below the ore unit, but they occur in places in the ore. They appear to be of relatively local origin.

The pebble beds vary considerably in their packing, grading laterally from well packed conglomerate through poorly packed conglomerate and pebbly arkose, to arkose with or without conglomerate seams.

Figure 12, a section from Stanrock, illustrates the typical situation which is more complex than can be shown without great detail.

The matrix of the conglomerate is composed essentially of quartz, sericite, and pyrite. Epidote is developed in minor amounts in grains and wormy intergrowths. Chlorite is rare.

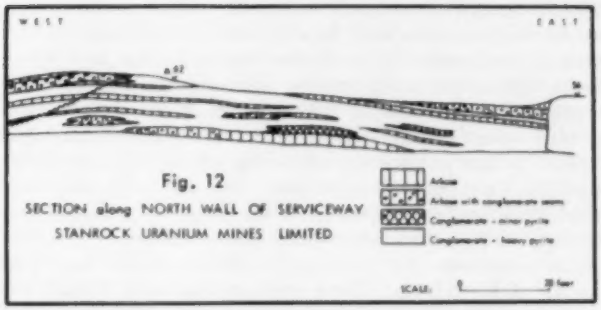
The quartz of the matrix occurs as grains, as bladed lamellar growths normal to pyrite faces, where it is commonly interleaved with slender sericite flakes, and in vermicular intergrowths.

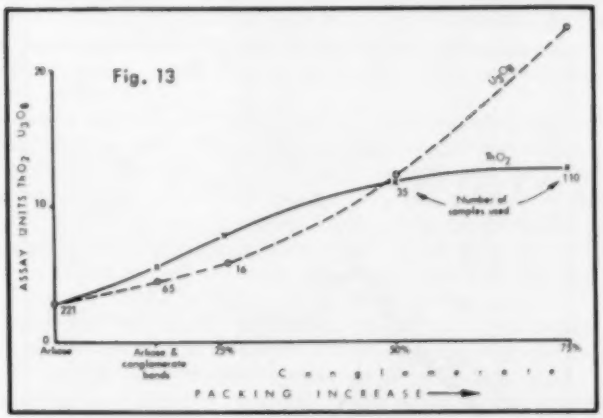
The quartz pebbles show strain shadows and exhibit cracks filled with regrowth quartz, sericite, and rarely, with subhedral pyrite. These pebble modifications and all of the matrix changes are considered to be the result of regional metamorphism that has lifted the grade of the rocks to that of the greenschist facies. This regional metamorphism occurred prior to the period of major faulting and prior to the introduction of late sulfide, pyrrhotite, chalcopyrite, sphalerite, and galena which, in part, appears to accompany the redistribution of some of the uranium.

The highest uranium values occur where the conglomerate is best packed excepting for the seams of thucolite, which can occur anywhere in or close to the ore beds. High pyrite content is indicative of high uranium values although high pyrite content does not guarantee high U_3O_8. As the pyrite content is highest where the conglomerate is best packed, this relationship between U_3O_8 and pyrite would appear to be an effect of packing rather than some intimate relationship between pyrite and uranium.

Figure 13 relates degree of packing of the conglomerates to uranium and thorium content. The rock character changes from arkose without pebbles on the left (221 samples) through arkose with bands of pebbles (65 samples) through conglomerate of increasing packing.

Figure 14 shows the character of variation of uranium content in continuous conglomerate beds at Stanrock. Variation can be more extreme than shown where the conglomerate pinches out or where thucolite seams become involved.





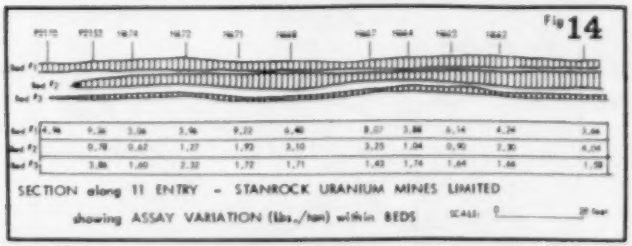


FIG. 12. Section along north wall of serviceway, Stanrock Uranium Mines Ltd.
FIG. 13. Relation of thorium and uranium content to the conglomerate development and its degree of packing. Assays are radiometric.
FIG. 14. Section along 11 Entry, Stanrock Uranium Mines Ltd., showing assay variation in beds of conglomerate. Assays are radiometric.

Figure 15 is a fence diagram illustrative of conglomerate unit distribution in the Milliken-Lacnor vicinity. The middle conglomerate is the main ore unit mined at Milliken, Lacnor, Algom-Nordic and Stanleigh. The lower conglomerate locally makes ore on the east side of Lacnor and in several areas on Milliken. The upper conglomerate unit approaches ore grade on the Stanleigh property. The mining unit involves a set of beds within which a mining width carries enough well packed conglomerate of good grade in one or more beds to carry interbeds of low-grade arkose or pebbly arkose. Mineable widths vary from about 5 feet to 35 feet at various localities, the latter widths reflecting conditions in which large volumes of conglomerate were laid down without thick intervening arkose bands.

Careful measurements of U_3O_8 grade, thickness, and bed character are made in many of the mines. These indicate that well defined trends exist within beds and within sets of beds. Thickness and grade are not directly

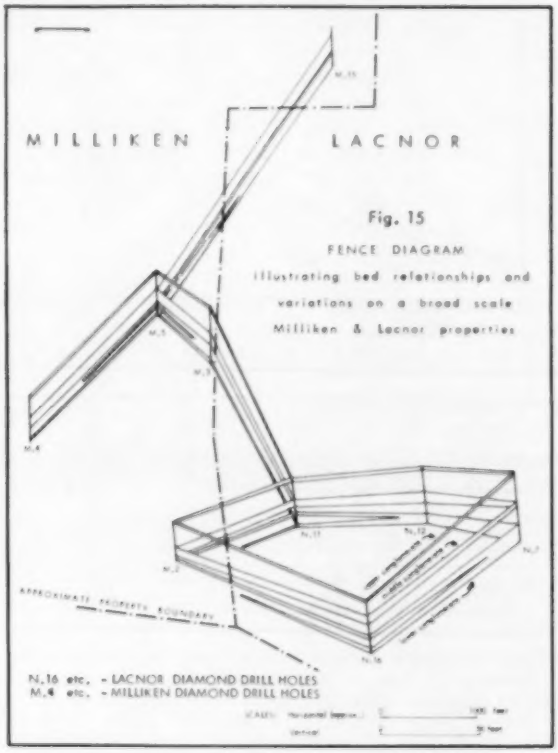


FIG. 15. Fence diagram illustrating ore zone relationships on parts of the Milliken and Lacnor properties.

correlative, although the trends developed from plotting thickness or grade coincide in direction. At Stanrock it is found that plots of the distribution of ThO_2/U_3O_8 ratios through the mining width also give trends coincident in direction to those developed on the basis of thickness and of grade.

Heavy Minerals in the Ore.—A variety of heavy minerals are described by various authors. Pyrite, "monazite," zircon, magnetite, uraninite and brannerite, the last two with their alteration products, we consider common.

A thorough study of the heavy minerals has recently been made by Milne (19). He lists the following heavy minerals obtained from four large samples collected across the width of the mining unit at one locality: apatite, biotite, carbonate, chamosite, chlorite (pale), diopside, epidote, fluorite, garnet, greenalite, grunerite, hematite, hornblende, ilmenite, muscovite, orthopyroxene, rutile, spinel (magnetite and chromite), tourmaline, zircon.

Among the radioactive minerals, he lists brannerite, uraninite, uranothorite, thucolite and a dark gray radioactive mixture partly composed of monazite which, for facility, we will call the "monazite" complex. Amongst the sulfides he found pyrite, pyrrhotite, sphalerite, molybdenite and galena, with the first two predominant.

Milne concludes, among other things, 1) that his heavy mineral suite is characteristic of a derivative from a metamorphic terrain in which iron formation was relatively important. "Grunerite, greenalite and chamosite are not very common minerals and as a group are even less common, except in iron formation." 2) that among his mineral suite are many normally considered as non-resistates such as diopside, hornblende and chrome spinel. He considers their presence to indicate short range transportation and rapid deposition and sealing of the sediments in which they are found.

Description of Some of the Minerals.—Pyrite, the chief heavy mineral, occurs in amounts up to about 15 percent of the rock unit and is found as euhedral, subhedral and rounded anhedral grains. It also occurs, although rarely, in stringers of massive character, some of which cut quartz pebbles. Except in these veinlets, which are of obviously late origin, the pyrite is always in discrete grains that commonly appear to be sized.

Pyrite occurs in seams both above and below the mineable ore unit as well as cutting it. It occupies bedding planes in the arkose forming bands of $\frac{1}{4}$-inch to $\frac{1}{2}$-inch in width made up of discrete grains. In places this pyrite has radioactivity associated with it, and at other places radioactivity is almost absent. Channel ways and cross bedding in the arkose within the ore unit are accentuated by these concentrations commonly with no trace of pebbles or a coarsening of grain size. In these cases in particular, the authors are impressed with the sedimentary character of the pyrite.

Arnold (13) describes pyrite with centers of leucoxene and believes that at least some of the pyrite resulted from sulfidization of pre-existing titaniferous magnetite. This may well be. That tremendous volumes of sulfur in one form or another, traversed the column, cannot be doubted by anyone observing the volumes of sulfide contained in fine fractures, as previously mentioned. However, such relict grains are at least not common. None

have been recognized in the numbers of thin and polished sections studied by the authors, and such occurrence is not reported by other workers.

Much of the pyrite is euhedral or subhedral even when it appears to be sized. That is, grains, all of similar size, run in bands. Is this pyrite regrown to euhedral habit during, and with the aid of, a period of metamorphism? Is it pyrite newly deposited on a pre-existing pyrite grain? Is it sulfidization of a pre-existing magnetite grain? The only evidence that appeals strongly to the writers is the general manner of occurrence of the pyrite with minerals of unquestioned detrital character and they believe the pyrite to be largely detrital although somewhat modified, as are the chief uranium bearing minerals and the feldspars and clays that originally formed part of the conglomerate matrix.

Brannerite has been described by a number of workers (21, 26, 32) as being the chief ore mineral of the conglomerate. Nuffield (21) describes it as ". . . reddish-brown grains of near microscopic size more or less altered to a dense white to yellowish-white radioactive product. The mineral is metamict and before ignition often gives the x-ray powder pattern of either rutile or anatase. After a momentary ignition at red heat, a pattern identical with the pattern of ignited brannerite from Idaho is obtained. . . ."

Whether the heating process merely returns the brannerite from its metamict state, or whether it actually synthesizes it, has been a problem. Patchett (23) has recently attempted to synthesize brannerite under controlled conditions and finds that this can only be done in inert atmospheres at temperatures above 2000° C. He cites this as evidence that momentary ignition could not synthesize brannerite and its place in the ore mineral assemblage appears secure.

Figure 17 shows a typical brannerite grain which in reflected light has a definite yellowish alteration product particularly heavy along the grain edges. The interior is a mass of opaque material and transparent needles of rutile (?). The rounded character of the grain is obvious. All brannerite grains seen by the authors are rounded to sub-rounded and show both the yellowish alteration product and a faint red coloration in oblique illumination, characteristic of the breakdown of iron-bearing minerals.

Uraninite is described by Traill (32) as occurring in angular to subrounded grains in the conglomerate matrix. He describes it as having a relatively high ThO_2 content of 6 to 10 percent. Two analyses of uraninite from Quirke Lake mines (29) give 6.3% ThO_2, 64% U_3O_8 and 5.9% ThO_2, 60% U_3O_8 respectively.

Thorogummite and anatase are reported as alteration products of brannerite by Traill (32) and by Rice (26). Rice believes the gummites to be of considerable importance as ore minerals and remarks about the Spanish American ore zone that, "The main ore horizon is predominantly composed of brannerite and secondary silica gummites, uranophane and soddyite. The gummite and brannerite are nearly in equal proportions, however, the uranium content of the gummites is 60–80 percent as compared to 30–40 percent in the brannerite."

Rice suggests also that the Quirke Lake mines are all rich in brannerite and gummite and relatively poor in uraninite as opposed to the mines on the south limb of the syncline.

Gow and Kaiman (12) reporting on Stanrock ore do not identify uraninite as an ore mineral. Stieff and Stern of the U. S. Geological Survey are reported to have found no brannerite in Pronto ore (*37*, p. 17) all of which lends some support to Rice's statement.

Open cracks in the ore and fracture zones commonly carry small, rounded, glossy, black globules of hydrocarbon with very low radioactivity. This material is locally called thucolite, although it does not correspond to the definition thereof (9) in that it has practically no radioactivity. This material commonly occurs with vuggy quartz or with pyrrhotite. It is obviously of late origin.

Cracks in bedding planes have yielded ¼-inch thick, black seams of material with a metallic lustre and high radioactivity, true thucolite. Impure samples from Stanrock Uranium Mines assay 49.3 lbs. U_3O_8 per ton. Pyrrhotite almost invariably accompanies it and both cut quartz pebbles close to seams along which major concentration occurs.

Powder patterns of the thucolite give prominent UO_2 lines identified as 111, 200, 220 and 311 with spacings of 3.13, 2.72, 1.93 and 1.65 respectively. The lines are somewhat diffuse. Figure 19 is a photomicrograph of a polished surface of this material. The ground mass in reflected light is light gray with a brownish tinge, faintly pleochroic. It is strongly anisotropic gray to brown. It resembles a sample described by Davidson and Bowie from the Isle of Man (8, p. 4). The angular shiny grains are UO_2. Other minerals are enclosed in the groundmass, chiefly pyrite, rounded monazite, and quartz.

Geochemistry of the Ore

Little has yet been done relative to variation in mineral content of the ore beds or to possible variations in the minerals themselves. Isolated sample studies have been made by a number of people (3, 12, 19, 21, 24) which do give information of value. However, the only regional work appears to be that of Rice, which is not yet in published form, and that of Roscoe (*27*). Preliminary regional work of any kind is thus of value.

Table 2 lists pertinent data from Stanrock Uranium Mines Ltd. The writers interpret this data to indicate that about 90 percent of the total rare earth content of the ores is in the mineral monazite. The rare earth is not extracted. Similarly about 40 percent of the ThO_2 content must be so contained.

Roscoe, in a recent valuable contribution (*27*) gives some detail on U_3O_8 and ThO_2 content of several of the minerals. He indicates that uraninite in the ores contains approximately 6% ThO_2 and 60% U_3O_8. Five brannerite assays average approximately 2.5% ThO_2 and 25% U_3O_8. Four monazite assays average approximately 5.6% ThO_2 and 1.5% U_3O_8. Monazite from mill tailings, on the other hand, averages about 2% ThO_2 and less than 0.1% U_3O_8. These last two sets of assays might be surprising in their disparity.

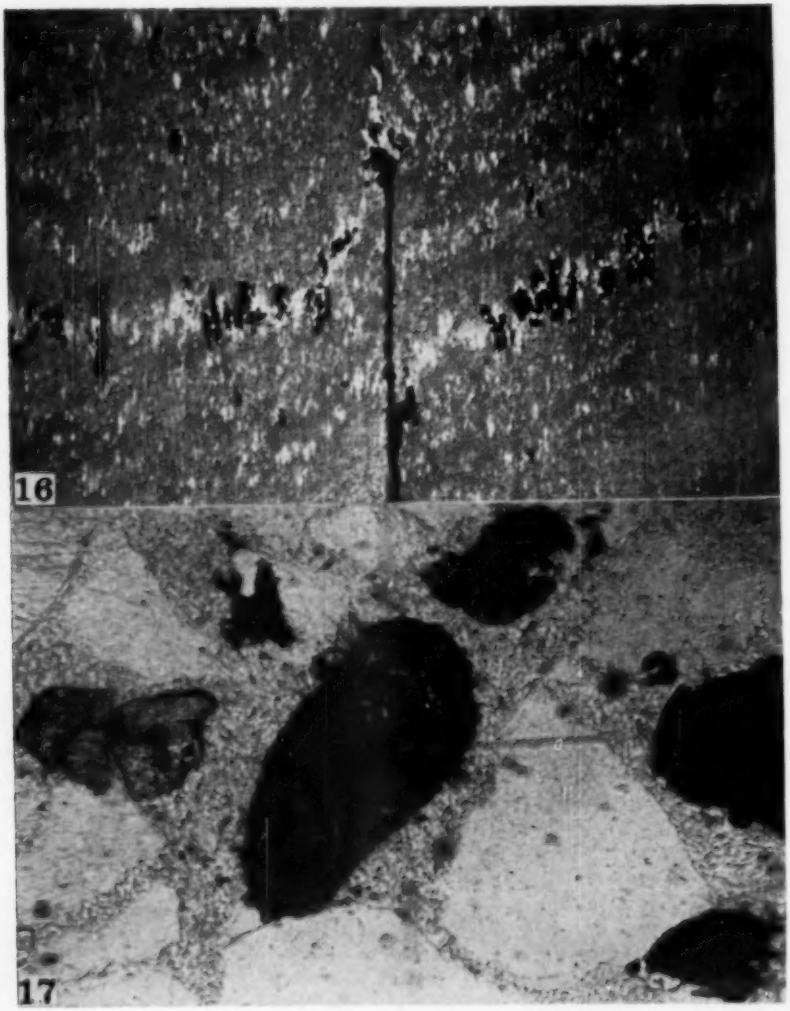


FIG. 16. Pyrrhotite and chalcopyrite (black) in fine fractures or cleavage in argillite, Middle Mississagi. The sulfides occupy fractures almost normal to bedding with the sulfide concentrated in the coarser grained bands. × 20.

FIG. 17. Brannerite grain whose edge is coated with a yellow alteration product and the whole grain is dusted with a pinkish alteration product. These alteration products commonly spill into the groundmass of sericite causing diffuse and ragged grain edges. Center of the grain is opaque material and acicular crystals of rutile(?). × 110.

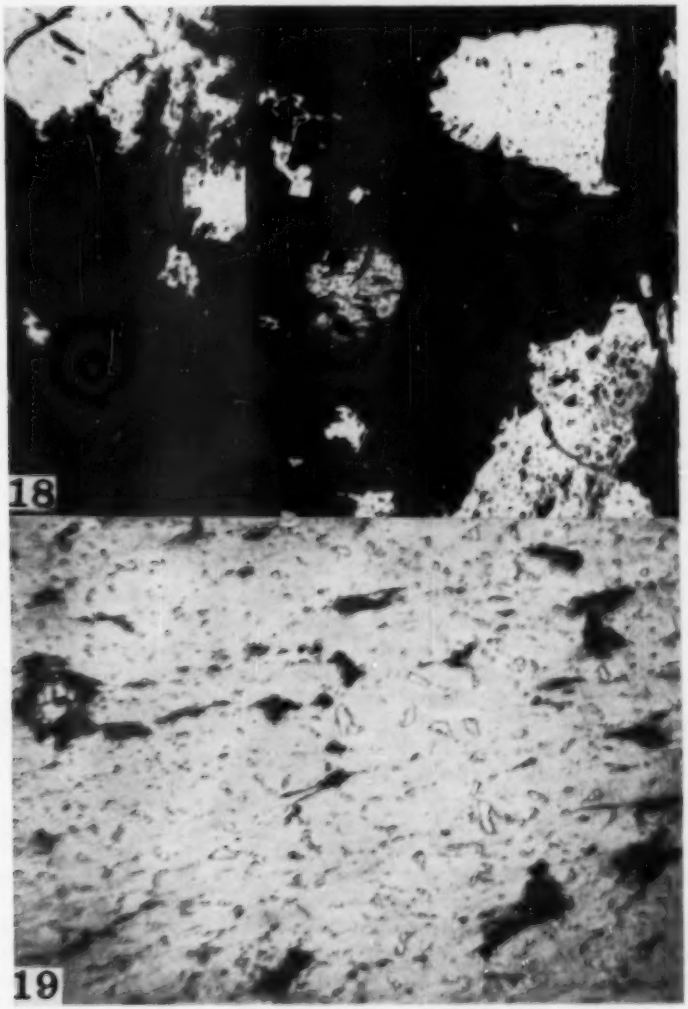


FIG. 18. Gray, rounded radioactive grain (uraninite) with euhedral to anhedral white grains (pyrite). × 60.

FIG. 19. Thucolite. The groundmass is hydrocarbon and the small angular grains are UO_2. Rounded grain of high relief, center left, is pyrite. × 60.

TABLE 2

TYPICAL THORIUM AND RARE EARTH CONTENTS OF MILL HEADS, MILL TAILS AND MILL EFFLUENT, STANROCK URANIUM MINES LTD. MATERIAL IN TAILINGS SOLIDS CONSIDERED TO BE ALMOST TOTALLY IN MONAZITE. ASSAYS BY CHEMICAL METHODS.

Head ThO_2	1.4 lbs./ton
Head Rare Earth	8.0 lbs./ton
Tailings Solids ThO_2	0.53 lbs./ton
Tailings Solids R.E.	7.33 lbs./ton
Tailings Effluent ThO_2	.87 lbs./ton
Tailings Effluent R.E.	.66 lbs./ton
% Thorium Unextracted	39%
% Rare Earth Unextracted	91%

However, Roscoe notes (*29*, p. 66) "It seems possible that much of the thorium and uranium in this monazite is in the form of uranoan thorite, either as solid solution or as segregations of metamict material." The writers prefer the second suggestion as the monazites of the ore are commonly not homogeneous as seen in thin section and such nonhomogenous materials are herein referred to as "monazite" complex.

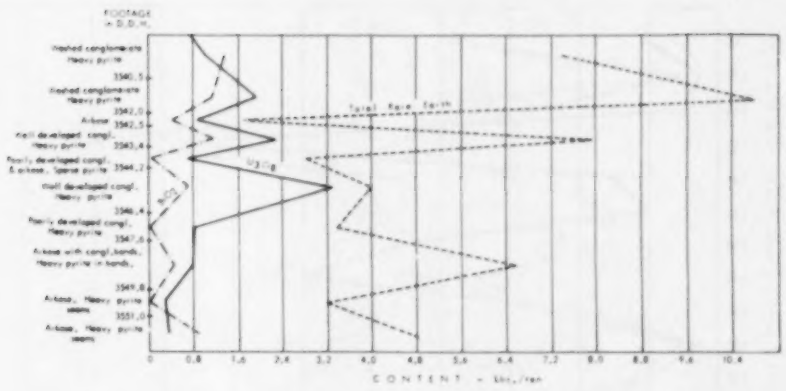
However, as Roscoe also noted (p. 66) ". . . the total thorium and uranium content must be regarded, for all practical purposes, as an integral part of the mineral," and as far as transport of the mineral grains or their origin is concerned, this is true. He states that ores from the mines on the south limb of the syncline have ThO_2/U_3O_8 ratios ranging from 0.12 to 0.4 and that ores in the Quirke Lake mines have ratios of about 0.5. He presents a table (*29*, Table 2, p. 66) indicating that an ore with a ThO_2/U_3O_8 ratio of 0.5 will carry 10 percent of its total U_3O_8 in "monazite" and that an ore with a ratio of 1.0 will carry 23 percent of its total U_3O_8 in "monazite."

1,500 assay samples from Stanrock Uranium give an average ThO_2/U_3O_8 ratio of 0.76. According to Roscoe's table approximately 16 percent of the uranium in the ore should derive from "monazite"—no small amount.

As previously described, the higher uranium values occur in zones of better packing and Figure 13 illustrates the principle. The left hand unit is arkose, commonly interbedded in the ore unit and lying in the foot and hanging walls. This figure was constructed from run of mine samples. As it is difficult in normal sampling to exclude conglomerate completely from the sample, the ThO_2/U_3O_8 ratio of the arkose shown is low. Individual ratios in material of this kind, commonly run as high as 5:1. The figure shows that with increasing pebble packing, the ThO_2/U_3O_8 ratio decreases.

Samples from top to bottom through ore units show this relationship in a gross way in that the ore unit itself, excluding variation within the unit, has a relatively low ThO_2/U_3O_8 ratio, but arkose above and below has high ratios. This relationship also appears to hold true in a regional way with the ThO_2/U_3O_8 ratio increasing down the paleoslope toward the southeast ends of the ore units.

Location	Ratio ThO_2/U_3O_8	Number of samples
Stanrock	0.76	1,500
Roche	1.74	11
Pardee	1.86	16



SECTION through STANROCK D.D.H. Z-7-48
Illustrating sympathetic variation in
U_3O_8, ThO_2 and total Rare Earth Oxides

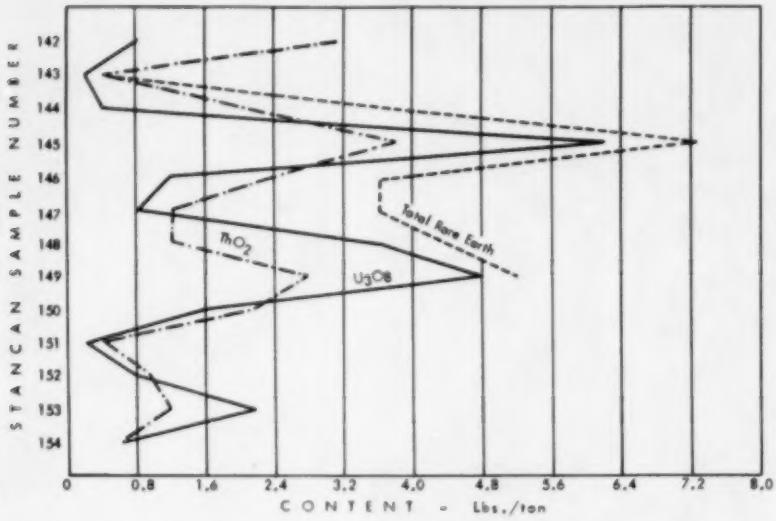
FIG. 20.

Roscoe reports an average ratio of 0.5 for the Quirke Lake ores. Stanrock is somewhat down the paleoslope from most of the mines and the ratio of 0.76 indicates a somewhat higher thorium content than usual. The Roche property is on the east side of Quirke Lake on the extreme edges of the Can-Met and Panel ore zones, at the southeast edge of conglomerate deposition as indicated by diamond drilling. The high ratio of 1.74 supports the suggestion of the previous paragraph.

The Pardee property lies east of the "zone of main ore occurrence" shown in Figure 2 and is considered to be well down the paleoslope. The high ratio, 1.86 supports the concept expressed above.

Sections through drill holes indicate the tight connection between the content of U_3O_8, ThO_2, total rare earth and the character of the beds involved. Figures 20, 21 and 22 are drawn from data acquired from diamond drill core. Of interest is the general higher ratio of ThO_2/U_3O_8 going from the Stanrock D.D.H. (Fig. 20) to the Stancan drill hole (Fig. 21) to the Roche drill holes (Fig. 22) in which case the average ratio is higher than 1. These holes are considered to be progressively further down the paleoslope. The intimate relation between the assays of different metals reflects a relationship between the minerals which the assays represent and a tight relationship between these minerals and lithology.

In each case, excepting that of the Roche diamond drill holes, assaying is by the fluorometric method for U_3O_8 and by a spectrographic method for rare earths and ThO_2. In the case of the Roche holes all assays are radiometric.



SECTION through STANCAN D.D.H. No.18-2A

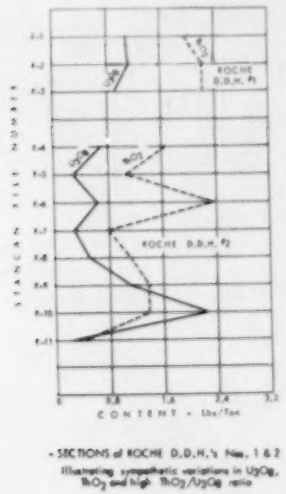
Illustrating sympathetic variation in U_3O_8, ThO_2 and total Rare Earth Values

FIG. 21. Section through Stancan D.D.H. 18-2A illustrating sympathetic variation in U_3O_8, ThO_2 and total rare earths.

Age of the Uranium Mineralization

Attacking the problem from a field geologist's point of view, the age of the quartz-pebble conglomerates themselves is of interest. They are undoubtedly older than the Cobalt series which lies much higher in the geological section with at least one unconformity in between. They are older than the basic dikes and quartz veins that cut both the Mississagi and the Cobalt series. As seen earlier, these dikes and quartz veins appear well dated at about 1,200 M.Y. Galena from Cobalt, Ontario, where mineralization is younger than the Cobalt series, give ages ranging from approximately 1,200 M.Y. to 2,000 M.Y. and averaging about 1,700 M.Y. (5). There appears to be no question that the conglomerates are older than 1,200 M.Y. and probably older than 1,700 M.Y.

That the basic dikes, the late sulfides and the quartz veins are younger than the uranium mineralization of the conglomerate seems certain from the details of their relationships observable in many of the mines. That there is no relationship whatsoever between these late phenomena and the uranium mineralization is indicated by the details seen in the mines and supported by



- SECTIONS of ROCHE D.D.H.'s Nos. 1 & 2
Illustrating sympathetic variations in U_3O_8, ThO_2 and high ThO_2/U_3O_8 ratio

FIG. 22.

their regional characteristics. They are never radioactive except in the cases of the chalcopyrite-pitchblende occurrences described above. The uranium mineralization of the Blind River conglomerate is also older than 1,200 M.Y. and probably older than 1,700 M.Y.

An approach from a geochemical point of view, and the ages of the minerals themselves, yields evidence that appears to confirm the above data, although the results are not conclusive and much more data are needed.

Using the Pb^{207}/Pb^{206} ratio, which appears to be the most suitable method for dating these older materials, it would appear that three ages of material are being identified: 1) material at Quirke Lake of age of 2,250 M.Y., 2) material from Pronto and from Quirke in the 1,300 M.Y. range and 3) material from Pronto at 630 M.Y.

Stieff and Stern refer to the material at 2,250 M.Y., "This old radiogenic lead may be from detrital minerals or pre-existing ore deposits in the basement

TABLE 3

AGES ON MATERIAL FROM BLIND RIVER ORES. REFERENCES REFER TO REFERENCE LIST AT END OF PAPER

Mine	Reference	Pb^{207}/Pb^{204}	Pb^{207}/Pb^{206}	Pb^{206}/U^{238}	Pb^{208}/Th^{232}
Pronto	30	1,400	520	340	345
Pronto	30	1,250	600	440	380
Pronto	30	1,350	570	400	410
Pronto	35	630	600	500	—
Algom Quirke	30	2,250	2,060	1,850	3,100
Algom Quirke	35	1,170	1,300	1,400	1,265

complex," (31). The authors agree that this is probably the case. The original uranium minerals in the conglomerate are detrital and of age older than the enclosing rocks.

It is of interest that one of the Theano Point pitchblendes gives an age of about 400 M.Y. (5, p. 62). Also, Kulp et al. refer to a pitchblende from Michigan as follows: "Uranium mineralization in the Upper Huronian of Michigan appears to have taken place about 400 plus or minus 20 M.Y. ago . . ." (18, p. 18).

It would appear that the Blind River uranium mineralization has been reworked at about 1,300 M.Y., the time of sulfide soaking and dike injection, and again at about 400–600 M.Y. at which time uranium mineralization appeared or was reworked at Theano Point and in the Upper Huronian of Michigan.

GENERAL DISCUSSION

Students in the Blind River field have largely been overwhelmed by the spectre of what might be called "The Witwatersrand Analogy." Because of the obvious similarities between the deposits and because of the argument, sometimes acrimonious, that has carried on over the origin of the Rand deposits, most students refrain, at least in print, from presenting any firm argument or displaying any strong conviction as to origin of the Blind River deposits. Holmes prefers a placer manner of origin, although with reservations. Roscoe takes no side although his papers suggest to the authors leanings toward a placer theory.

Authorities in the general uranium field, with little experience with the Blind River rocks, have not been so reticent. C. F. Davidson is convinced of a hydrothermal origin. Stieff and Stern suggest that the uranium mineralization may be Paleozoic, which implies a hydrothermal origin, this based on age determinations on specimens from two mines in the area.

No one has yet stressed the differences between the deposits of the Rand and Blind River, or the fact that because of a generally simpler geological situation in the latter area, it is much more likely that studies in Blind River will yield evidence bearing on the Rand than vice versa.

It should be noted that the heavy mineral suite at Blind River is much simpler than that at the Rand. The minerals are all those that could originate, without complex juggling, from a typical Precambrian metamorphic terrain cut by quartz veins and granite; indeed, from a terrain very similar to that on which the Huronian rocks of the Blind River area lie. Thus, in apparent contradistinction to the Witwatersrand situation as represented by Davidson (7, p. 672) the likely consorts of placer uraninite are present in the Blind River reefs and the minerals which normally accompany uranium of hydrothermal origin are absent, except in cases where they give obvious evidence of their late origin.

Gold is not present in the Blind River rocks except in sporadic traces. Its manner of occurrence is not known. In the Rand, of course, gold is the prominent mineral and most of the arguments on the subject of Rand origin become involved with the physical character of the gold.

The bulk of the uranium in the Rand is contained in carbonaceous material similar to thucolite. Both pitchblende and uraninite would appear to be present. The chief uranium minerals in the Blind River ores are brannerite and uraninite, the uraninite being coarsely crystalline and with a content of about 6% ThO_2. Carbon complexes, although widespread, are very minor in amount. Pitchblende is rare.

Metamorphism is described by some authors as being significant in the Rand. Ramdohr says (25, p. 10) "This has led locally to the complete melting of those rocks which are susceptible to melting, accompanied by the formation of pseudogranophyre. Moreover, this igneous activity repeatedly created pseudohydrothermal conditions over the whole area for long periods and likewise gave rise to silicates, especially chloritoid, which can be looked upon as characteristic of the metamorphic grade of the mezazone." No one has suggested activity of this scale at Blind River where the rocks, while normally recrystallized to a degree, are low in the green schist facies with abundant sericite and rare pale colored chlorite, and with a little rare epidote. Assuming that Ramdohr's description of Rand metamorphism is correct, even to a degree, it is obvious that nothing comparable on a regional scale is seen at Blind River and the problem of mineral origin, uncomplicated by regionally elevated temperatures and pervasive metamorphic fluid movement, should be a simpler one to solve. It appears to be so.

It should be pointed out here that the authors recognize the general similarity between the Witwatersrand and Blind River and are familiar with much of the literature that favors a placer origin for the Rand ore deposits. Our concern here has been to show that evidence which complicates the problem of origin on the Rand has no significance at Blind River because of differences between the deposits.

The major uranium-bearing minerals at Blind River occur in detrital-like sub-rounded to rounded forms. This is particularly true of the "monazite" complex and brannerite, which, as far as the authors are concerned, occur in no other way. Uraninite also occurs in sub-rounded grains, but angular grains have been described. Physically the minerals appear to be detrital.

It has been argued that uraninite does not have the ability to withstand transportation and deposition. A recent contribution by Koen (17) proves that uraninite is physically quite stable. Using sized uraninite from the Witwatersrand (0.044 mm to 0.074 mm) and sized, rounded monazite from a wind blown sand (0.044 mm to 0.074 mm) in a high speed attrition cell, he produced results shown in Table 4.

TABLE 4

CUMULATIVE PERCENTAGE LOSS OF URANINITE AND WELL ROUNDED MONAZITE (AFTER G. M. KOEN)

Period of treatment	Uraninite	Monazite
1 hour	33.0	37.0
2 hours	53.5	57.1
3 hours	63.8	69.9
4 hours	70.0	80.0
5 hours	80.2	85.1

In all of his attrition experiments uraninite proved to be "capable of resisting mechanical wear at least as successfully as monazite—a mineral that commonly forms an important allogenic constituent of black sands. If monazite can survive the physical rigors of sedimentation, uraninite can do so too" (17, p. 8).

There is no reason why the major uranium-bearing minerals could not be detrital.

The distinction between uraninite and pitchblende is commonly made, as described by Roscoe:

> to describe the two distinct varieties of uranium oxide which are found in nature, both of which have a UO_2-type crystal structure. Pitchblende contains less than 0.1% of thorium and rare earth oxides and is the typical urania mineral found in hydrothermal deposits. Uraninite, on the other hand, contains appreciable amounts of thorium and rare earth oxides (usually more than 1.0 percent) and is the variety of urania found in pegmatites, migmatites and granites.

It might also be added that an unground piece of pitchblende gives a typical powder pattern with smooth arcs indicating very fine grain size or crystallite size, while a similarly unground piece of uraninite gives discontinuous arcs indicating large crystallite size. The Blind River mineral of composition UO_2 is typical uraninite with approximately 6% ThO_2 and quantities of rare earths, as has been earlier noted. It is thus distinctly different from the pitchblendes at Cobre Lake or Theano Point. The uraninites are related to pegmatoid assemblages rather than to hydrothermal assemblages. This is also true of both the "monazite" complex and brannerite, which on the basis of associations described in the literature, are much more likely to be associated with granites and related rocks than to hydrothermal veins or leakage. No pegmatites or granites cut the Huronian of Blind River.

The evidence from these minerals then appears to lead through a detrital transport to a pegmatoid or granitoid parent rather than through some unguessable mechanism to a hydrothermal source below.

Quartz pebble conglomerates are locally developed over much of the basin area. In most cases they are only a few pebbles in width and although radioactive, the bulk of the radioactivity is due to thorium. One distinctive occurrence of quartz pebble conglomerate, of appearance identical in the hand specimen or on the outcrop to the Blind River ore zones, occurs at the southwest corner of Lake Wanapitei to the northeast of Sudbury. At this locality a bed of radioactive conglomerate, 5 feet to 8 feet in thickness, and with a thin quartzite at its base, lies on the basement complex of greenstone, granite, diabase and rhyolite. The showing is faulted in a complex way with about a 1,500 foot length of sediment outcropping on the shore. One thin section of conglomerate from this exposure showed a mineralogy similar to that of Blind River, although the only radioactive minerals found were monazite and the "monazite complex." Any theory of conglomerate origin has to explain this occurrence and any discussion of origin of the uranium minerals cannot ignore it.

As seen in Figure 2, the only conglomerate zones of thickness and grade such as to be economic lie within a north-northeasterly trending belt within

which each zone has a southeast trend. This north trending belt is of interest because, if as earlier suggested, the conglomerate zones are of differing ages, the results of temporary flushing of coarse detritus into a transgressing sea, it is a coincidence of a very high order that they would line up in this fashion unless the orientation of the belt had some significance.

The broadly distributed cross bedded arkose and sub-arkose of the Matinenda formation can hardly be considered completely alluvial as has been commonly suggested. More likely they are the product of a northward transgressing beach environment at which detritus was plentifully supplied by small streams from the north. Locally, larger rivers carried heavier detritus which was more quickly buried than the reworking material on the beach front. The conglomerates were undoubtedly less well sorted than the normal arkose, witness the distribution of heavy minerals with light minerals in the same size range and the abundant sericite, probably derived in part from clays. The conglomeratic ore zones are the best examples of such a large river, the conglomerates probably developing in subaqueous deltaic conditions off the river mouth. The yellow arkose envelope represents the finer grained detritus carried off the edges of the delta. This material continued to flush into the subaqueous environment when the major stream no longer carried the coarse detritus of the conglomerates and thus built up above and off the edges of the conglomerate zones.

The northerly trending belt in which the conglomerates are developed is thus explained as the direction of the major paleostream, the mouth of which retreated sporadically northeasterly as the sea advanced.

The southeasterly trend of the ore zones may be governed by off-shore currents moving detritus steadily to the east. The thickening of the Matinenda formation at the ore locales is probably due, at least in part, to thickening of sediment on the delta and not alone to thickening in basement depressions as has been believed commonly. Basement depressions, of course, do exist. The authors are not convinced that their sole trend is northwest or even that the major trend is northwest. Isopachs of the Matinenda formation do not alone prove basement depression and careful studies on the basement are required.

That the generally transgressing sea occasionally regressed is witnessed by the development of the sheet-like, radioactive, polymictic conglomerate of the Matinenda formation. This conglomerate has been described as cross cutting to the south in the Stanleigh vicinity and as channeling an ore conglomerate section in the Crotch Lake area. Its content of chloritic material suggests a local origin, possibly to the south, while its radioactive content and its quartz pebbles may be partly derived from previously deposited ore conglomerate.

Occasional stability with long continued reworking is well illustrated by the fine grained equigranular quartzite well developed, and used as a marker horizon, at about 12 feet below the ore conglomerate on the Stanrock and Spanish American properties.

Continuing advance of the sea to the north is reflected in the argillite, siltstone and graywacke of the Nordic formation, indicating a deeper submergence

of the south limb of the syncline. The Nordic unit on the south limb is thus the time equivalent of material of the Matinenda formation being deposited on the present north limb or further north in an area eroded prior to deposition of the Middle Mississagi.

Middle Mississagi time begins with either rapid uplift to the north coupled with submergence of a larger area, or a general tilting to the south of an area including the present basin area. A general outpouring of the sheet-like polymictic conglomerate and graywacke at the base of the Middle Mississagi took place. Deeper water conditions are then again seen through the rest of Middle Mississagi time over the entire presently known basin.

CONCLUSIONS

The authors believe the conglomerates of the Blind River area to be part of a sequence of detrital sediments laid down in a beach and delta environment during a period of cyclical fluctuation of the land mass and a generally northward transgressing sea. The ore conglomerates are discontinuous wedges or sheets in the section and younger in age from south to north. The source area of the sediment is considered to be a metamorphic terrain cut by granites, pegmatites and quartz veins, not dissimilar from the basement rocks on which the Huronian lies in the Blind River area. At least some of the detritus is of relatively local origin.

The age of the conglomerate and its associated heavy minerals is considered to be older than 1,200 M.Y. and probably older than 1,700 M.Y.

The uranium minerals of the conglomerates are considered to be detrital and for the following reasons:

1) They normally have a detrital aspect.
2) They exist within a normal detrital assemblage and occur in the same way as other detrital minerals.
3) They have attributes apparently militating against a hydrothermal origin. Uraninite with its coarsely crystalline character and high thorium content has affinities with pegmatite and granite rather than with hydrothermal veins. The "monazite" complex and the branneriite are more likely bred in a granite or associated rock than in a pervasive hydrothermal environment.
4) There are no hydrothermal effects such as might be expected to be connected with the formation of high temperature uranium bearing minerals.
5) There is obviously no connection between the uranium minerals and sulfides, quartz veins, or basic dikes, nor any connection with faults.
6) The ThO_2/U_3O_8 ratio varies in manner explicable by syngenetic theory as the normal gravity grading taking place in detrital sediment with light minerals (monazite) moving farther than heavy ones (uraninite). This cannot be explained by hydrothermal theory.
7) The Wanipitei Lake conglomerate can be explained as a normal detrital deposit from the source area to the north, or northwest. In view of the large number of conglomerates elsewhere in the geological suc-

cession, that do not have pyrite in volume and radioactivity associated with them, it is too much of a coincidence that hydrothermal activity would search out this typical Blind River type conglomerate, approximately one hundred and twenty miles from Blind River, and mineralize it in fashion similar to the Blind River mineralization.

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Many geologists of the area have facilitated the writers' access to information, have pointed up evidence bearing on the distribution and origin of the ore and have freely discussed the area's problems, all of which the authors acknowledge gratefully.

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GMX Corporation,
Toronto, Canada,
Aug. 26, 1959

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PATTERNS TO ORES IN LAYERED ROCKS[1]

GEORGE W. BAIN

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[1] Presented at the annual meeting of the A.I.M.E. and Soc. Econ. Geol., New Orleans.

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ABSTRACT

Distribution patterns of syngenetic ore bodies in layered rocks correspond in area, symmetry, and metal variation with the rock facies structures. Distribution patterns of epigenetic ore bodies either correspond to antecedent and contemporary tectonic structures or deviate systematically under their influence. Many deposits have metallization, initially syngenetic, redistributed slightly by groundwater of varied origin, and these occurrences acquire a tectonic asymmetry while retaining their syngenetic facies limitation. Selected examples of intensively studied deposits are cited and examined critically, and criteria are presented to indicate the syngenesis or epigenesis of metallization as distinct from mineralization.

INTRODUCTION

PATTERNS to occurrence of ore are important both to appraisal of resources for a region while it is yet in a youthful stage of development, and also to augment depleted reserves at minimum expense during maturity. Furthermore coincidence of mineralization distribution with either some particular syngenetic feature or some epigenetic structure in sedimentary or other rocks of surficial origin can be a deciding factor in arriving at a scientific estimate of mineral deposit origin. In yet another way, coincidence of ore patterns to patterns of other geologic features is an important aid to exploration of a mineralized area.

GENERAL STATEMENT

The great number and greater proportion of the world's mineral products come from surficial rocks, commonly former sediments but in places volcanic materials. These hosts have stratified continuity; many contained ores have a continuity that follows a facies of the host or at least mimics it; elsewhere ore distribution is patterned on tectonic or plutonic structures that occur only locally in the host. The dominating influence over a pattern needs to be appreciated early in the development of a mineral district in order to direct major exploration where it can have most hope for fulfilment of its objective.

EXAMPLES OF OBVIOUS PATTERN

Complex examples could be selected but such selection would defeat the purpose of this presentation. Two simple well known instances will illustrate the application of patterns to solution of some ore search problems and the more controversial instances will be introduced as more complex assemblages are set up serially. Both examples are in conglomerate hosts, formed under similar physical conditions carrying native metal ores which were emplaced in the host with very different patterns under radically different conditions.

Stream Gravel Host

The stream gravel hosts for ore which are selected include the Tertiary age auriferous gravels of the Sierra Nevada and the Calumet and Hecla conglomerate of Michigan.

Alluvial Emplacement.—The Tertiary auriferous gravels of the Sierra Nevada (20) occupy former river channels radiating outward from a mineralized domain centered near Lake Tahoe (Fig. 1). Lava flows cap nearly all of the gravels, which accumulated on a relatively mature land surface of about Miocene or early Pliocene age. The gravels have an assemblage of heavy refractory minerals and carry in addition considerable iron sulfide. The entire region has been inclined westward at about 3.0 percent slope. The Mayflower Channel (Fig. 2) is a well documented, reasonably typical example that is nearly parallel to the strike of the Sierra uplift. Average gold content was about 7 pennyweights per ton; rich parts are just "down current" from the bends in the old channel, ore is displaced slightly towards the concave bank and is symmetrical with respect to axis of current flow; three bends are recorded, each with rich parts and all are deflected to the concave bank without regard to the 3 percent tectonic dip of the stratification which is transverse to the channel axis. Here the value distribution follows a sedimentation pattern and was not modified by any later agency such as the tectonic disturbance.

Solution Emplacement.—The Calumet and Hecla conglomerate in the upper peninsula of Michigan was a channel deposit laid by a stream flowing southward from the "Killarney Mountains" of Canada. The conglomerate dips about 40° northwestward; it is mineralized with native copper, and arsenides. Mineralization is asymmetrical to the axis of the channel; greatest amount of copper per square foot of bed is projected up-pitch along the channel axis (Fig. 3) and greatest amount of copper per ton is deflected up-dip (Fig. 4). In a positive sense, value distribution follows a tectonic pattern (pitch and dip) imposed on a particular sedimentary facies; in a negative sense, values decline conspicuously down-pitch and down-dip from the channel gravel facies; asymmetry to distribution of copper relative to host features is ascribed generally to arrival of the mineralization after the tectonic event modified the symmetry of the host.

Generalization.—The instances are far removed from the controversial list of ores in sediments and illustrate a principle of pattern symmetry in evaluating a deposit economically and genetically. The Mayflower Channel has sym-

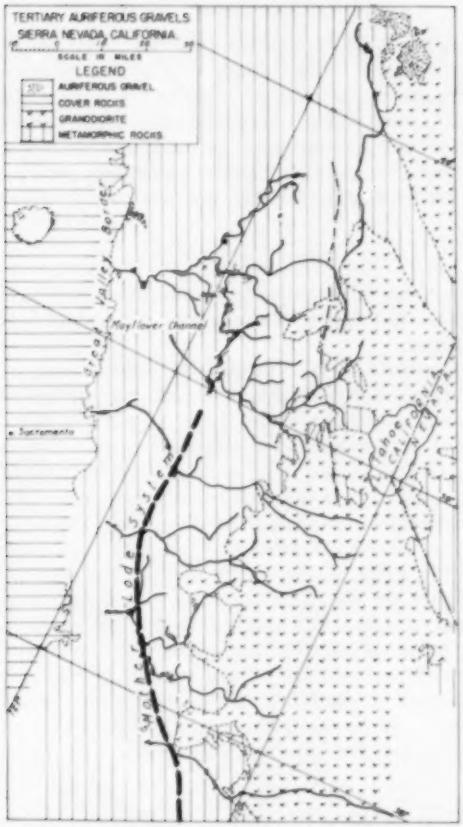


FIG. 1. Radial distribution of Sierra Nevada alluvial gold about Lake Tahoe.

metrical coincidence of ore with host facies and ore can be presumed to have been emplaced before the host received its tilt to westward. The Calumet and Hecla conglomerate channel has only partial coincidence of ore to host facies, and exhibits such paralytic asymmetry of ore to host that production of ore down-dip from the axis of sedimentation was minor. Ore can be presumed to have been emplaced after the host was tilted to slope northwestward.

Syngenetic mineralization, which is facies influenced, has major features coincident with syngenetic patterns of the host and disregards tectonic patterns. Major features of mineralization coincide with syngenetic patterns and are displaced strongly and generally asymmetrically on the tectonic patterns where mineralization is epigenetic. Epigenetic redistribution of a

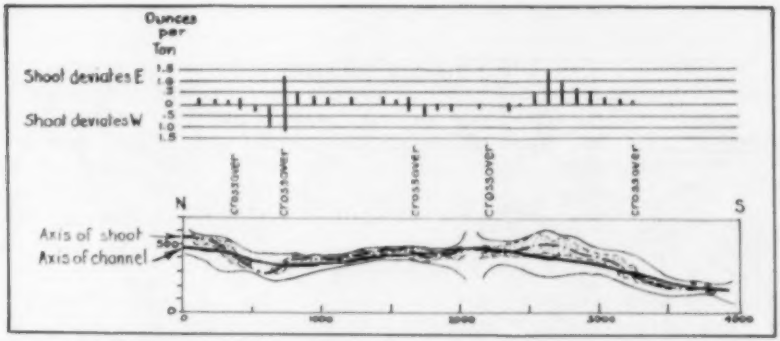


FIG. 2. Payshoots occur just downstream from meander turbulence in Mayflower Channel, California.

syngenetic deposit generally introduces some asymmetry but not enough to mask the original pattern.

Identification of Host Facies

The host facies may pass unrecognized due to distracting diversions by error either from the origin point of view or from inadequate subdivision point of view. The Witwatersrand has been blamed on everything from glaciers (*32*), to bathing beaches (*22*), to the exhalations from the infernal

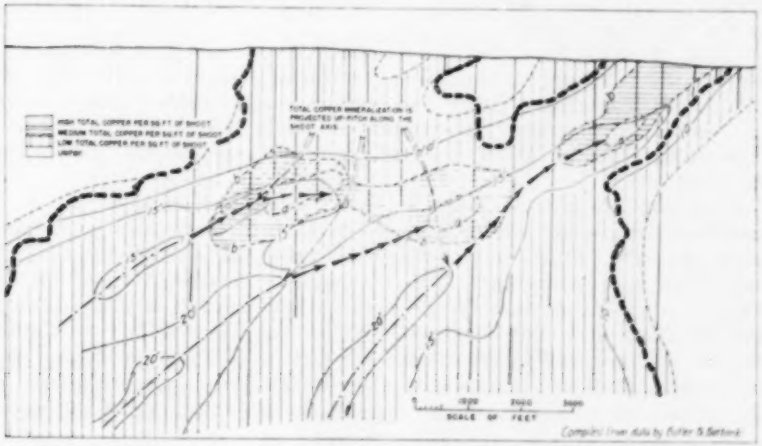


FIG. 3. Up-pitch projection of maximum total copper in Calumet and Hecla Conglomerate.

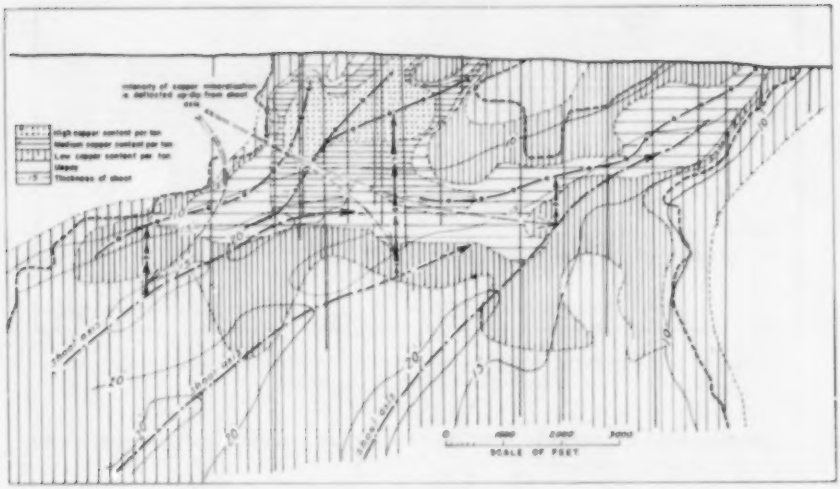


FIG. 4. Up-dip projection of maximum copper per ton in Calumet and Hecla Conglomerate.

regions (12); the areal case will be considered later but now it is necessary to clear up the matter of host facies identification.

Morainal detritus left by continental glaciers, even after assortment as on New England's beaches, has a much greater size distribution range and angularity of form to sand than is encountered in the reefs of either the Rand or the Orange Free State.

Beach alluvials have the heavy minerals concentrated at the top of a stratum and at the uprush line facies on a beach, generally a sand. They are in a single narrow band rather than multiple parallel strips. This is found on beaches with moraine provenance (Gillespie's Beach, N. Z.), or delta provenance (Rosetta Mouth of the Nile), or dune provenance (Stradbroke Is., Queensland).

River alluvials have the heavy minerals concentrated near the bottom of their host stratum and may be in several parallel strips representing different scour channels. Furthermore only theory says that such sediments lack sulphides; both authigenous and allothigenous sulphides occur in the alluvials of Fairbanks, the Sierra Nevada, South Island of New Zealand and the beaches of New England. Of the many gravels laid in a river channel only the well assorted basal scour facies is highly productive and of the many sands in a beach deposit only the top layer of a beach alluvial at the uprush zone of a particular aggradation cycle has significant heavy mineral.

A series of limestone beds in the Tri-State district choose to be chertified and mineralized whereas other almost identical strata are not. Here a rock

type is not the sole feature of a facies; a facies is the result of an entire environment that imparts grain form, diluents, cementation, limited continuity and accessibility; each becomes an important item in the pattern, which unfortunately often goes unrecognized. Accessibility as provided by shear zones and jointing is an important part of facies in the Tri-State district.

As a general principle, facies is the expression of contemporary events in the record; these may be either metal concentrating or influencing upon separation. Facies may affect later episodes involving elasticity, permeability, and chemical susceptibility which are important to epigenetic mineralization.

THE CONTROVERSIAL CASES

The two preceding examples are deposits on which reasonable unanimity of opinion exists and the pattern to distribution, both areal and in depth, is established. Their ores attend a particular facies of a relatively large and more or less homogeneous looking rock body. In places the deposit is coextensive with the facies and should be considered syngenetic. Elsewhere the deposit is in the facies but coincides with intercept by a specific tectonic structure or "facies" of tectonic structure and should be considered epigenetic. The economic mineral components in these epigenetic deposits may be indigenous or immigrant. However in every instance, a facies such as lava flow front, river channel gravel, beach sand, or "coral" sandbar has its own distinctive pattern; recognition of even a small part of a pattern as coincident with an ore pattern can be important to appraisal of the resources and trend to a new mineral region.

The following examples have the pattern to ore distribution established with as good dependability as is possible before exhaustion of the deposit, and the variety of syngenetic facies and epigenetic structures are reasonably well known; yet they constitute highly controversial subjects. Their facies patterns doubtless can rile the geologist and settle the geology.

These examples include:

1. Shale siltstone hosts
   a. The alum shales of Sweden.
   b. The Kupferschiefer of Germany.
   c. The Congo-Rhodesia copper belt.
2. "Conglomerate" hosts
   a. The Witwatersrand.
   b. The Orange Free State goldfield.
   c. The Blind River uranium area.
   d. The Colorado River Plateau uranium deposits.

THE SHALE–SILTSTONE HOSTS

The first major group of patterns to be considered are from deposits in shale and siltstone hosts; characteristically these are initially the most uniform sediments known and they carry a considerable variety of metals. The Chattanooga black shale on the margin of the central platform of North America, shales of the phosphatic member of the Phosphoria formation of

the northwest states and the Swedish alum shales of Europe are excellent examples; these show relatively uniform metal patterns but even here some initial variation and secondary redistribution on tectonic patterns is evident. As studies are extended to the Kupferschiefer of central Germany and the Katanga system of the Congo-Rhodesia border, intensification of the tectonic pattern influence upon metal distribution coincident with rising metal content becomes emphasized; the entire cumulative frequency graphs for metals in a deposit, which are very similar in a sedimentary deposit (28, 6), become progressively more divergent in the Kupferschiefer and the Congo-Rhodesia border ores.

THE ALUM SHALES OF SCANDINAVIA

Metals in the Alum Shales of the Peltura Zone

The alum shales of upper Cambrian age of the Peltura scaraboides zone of southern Sweden carry V, U, Mo, Ni, Co and Cu in more than hundredths of a percent and the amount varies systematically from place to place (Table 1). The Dictyonema shales, higher in the series, carry more of all metals, except U which is less than in the Peltura beds.

The Sedimentary Pattern

The alum shales of Cambrian age of the Peltura zone were deposited in greatest thickness in a gulf east of Vanern and north of Vettern, which opened southward into Skane and westward into Norway (Fig. 5). The shale thickness is up to 16 ms in Narke, 4 to 9 ms east of Vettern and is absent on

TABLE 1

METAL DISTRIBUTION, PELTURA ZONE, ALUM SHALES, SCANDINAVIA

*	Kinnekulle[1]	Narke[1]	Billingen[1]	Ostergotland[2]	Oland[2]	Skane[3]	Bornholm[1]
V	0.075	0.125	0.10	0.05	0.060	0.15	0.03
U	Present	0.025	Present	0.013	0.009	0.008	Present
Mo	0.025			0.015	0.012	0.015	
Ni				0.01	0.009	0.025	0.005
Cu				0.01			0.010
Co				0.004	0.003	Present	0.001
Cr							0.001
Zn							0.002
Pb							0.004
W	Tr.					Tr.	

* All elements in this list present in all areas but amount not stated in the literature.

[1] N. Sundius, Oil shale and shale oil industry. Sver. Geol. Under., Ser. C, 441, pp. 42–43, 1941.

[2] A. H. Westergard, Borings through the alum shale beds of Oland and eastern Gotland 1943. Sver. Geol. Under. Ser. C, 463, pp. 6–7, 1944.

[3] A. H. Westergard, Borings through the alum shale of Skane 1941–42. Sver. Geol. Under. Ser. C, 459, p. 13, 1944.

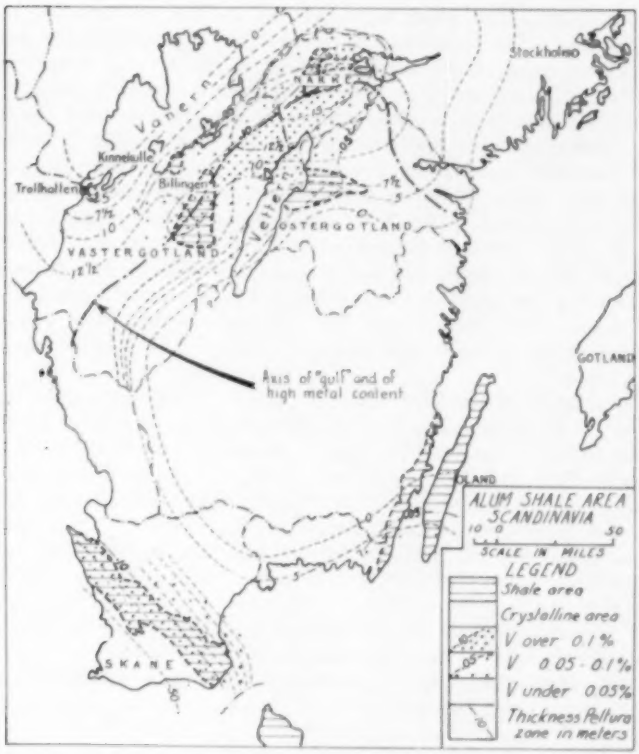


FIG. 5. Location of maximum metal content of Swedish Alum Shale in center of basin.

Gotland; the horizon is 10 to 13 ms thick on Billingen and eastern Kinnekulle but is almost absent at Trollhatten at the outlet to Vanern; the beds increase to over 40 ms thickness in Skane lying to southward from the Trollhatten, Vettern, Gotland axis. The total shale thickness represents accumulation over a very long period at an extremely slow rate. General metal content is greatest in the middle of the "Gulf"; however, it should be pointed out that vanadium is abnormally abundant in the thick shales of Skane. Within the gulf, facies patterns for thickness of shale and to metal content coincide, and the metal content may be considered as dominantly original.

The Metal Pattern

Before starting to outline the patterns of the metals in the Alum Shales, it is necessary to have a better understanding of their associations. The metals are not distributed homogeneously or even uniformly; a thick vein of hydro-

carbon at Ulanda had about 0.3% V and another at Karlsfors had even higher content. The shales have between 1 and 5 percent of concretion-like hydrocarbons called kolm carrying about 0.5% U and considerable V. These hydrocarbons are often referred to incorrectly as sapropels. Many kolm nodules have shale bedding continuous through them and the high ash content (generally 25%) is due to the occluded shale residue. The kolm are mostly lenticular nodules but a considerable part are platy masses about 2 inches thick which extend for several feet at about this thickness to within half a foot of their end. The shale bedding planes bulge around the kolm just as they do around the lime concretions in the same formation. This relationship shows that the kolm was not a stratum of the original sediment, and therefore not a sapropel, but is a polymerized hydrocarbon formed in place at a later time. Thus no evidence yet adduced indicates that any metallic component of the kolm existed there originally. The best clue lies in the metal patterns.

The vanadium content for samples changes; for Ostergotland it is 0.03 to 0.07% V, in Skane it varies from 0.04 to 0.21% V, and on Bornholm is less than 0.05% V, at Karlsfors and Billingen it is 0.09 to 0.11%, and in Narke runs 0.05 to 0.20% V, whereas at Kinnekulle in the west it is only 0.075%V. The shales of Skane have 0.01 to 0.02% Mo, 0.01 to 0.04% Ni and up to 0.013% U as well as some cobalt and tungsten. The Ostergotland deposits run 0.015% Mo, 0.007 to 0.016% Ni, 0.002 to 0.006% Co, 0.005 to 0.015% Cu and about 0.018% U. The values listed in Table 1 are the best average that can be given now.

The highest average V and U contents are from Narke in the middle of the gulf; Billingen at the deep southern outlet to the gulf has the next highest content; the shallow edges from Kinnekulle to Trollhatten and in Ostergotland and Oland have lesser content.

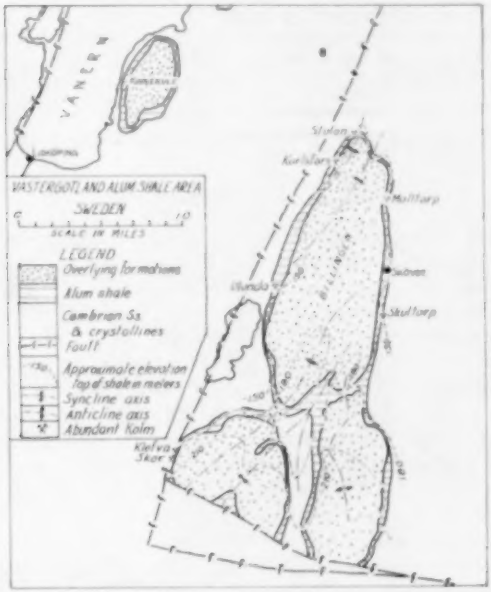
Tectonic Pattern Influence

The strata are nearly horizontal but an arch of about 30 ms closure over about 5 km width extends under the west side of the Billingen Berg at Stolan and Karlsfors (Fig. 6). Along this axis the kolm nodule frequency is much higher, and the metals content rises also. A second axis goes through the Mossberg and has high kolm freqency at Skar and Kleva; a third axis passes through Gullhagen and Skulltorp and again kolm freqency is high. Even in the most sedimentary of deposits some redistribution of hydrocarbons and their contained metals has occurred but without either hydrocarbon or metal leaving its originating bed in great amount except at Karlsfors and Ulunda.

THE KUPFERSCHIEFER OF GERMANY

General Features and Stratigraphic Pattern

The copper shale encircles the Permian age salt basin of Germany. Metallic mineralization is principally on the periphery of the Harz Mts. and the Richelsdorf Hills, and is the largest copper deposit in Central Europe.


VASTERGÖTLAND ALUM SHALE AREA
SWEDEN
SCALE IN MILES
LEGEND
Overlying formations
Alum shale
Cambrian Ss
& crystallines
Fault
Approximate elevation
top of shale in meters
Syncline axis
Anticline axis
Abundant Kolm
VÄNERN
Kinnekulle
Mullsjö
Skövde
Skultorp
Hunnebo
Kinnekulle
Kinnekulle
Kinnekulle

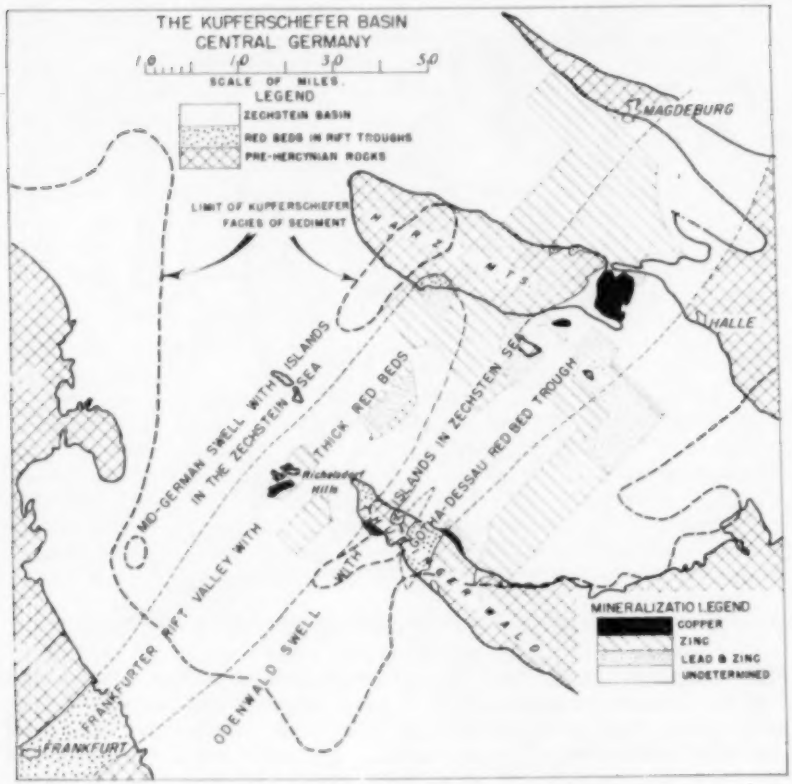


FIG. 7. Structural segregation of metals in Kupferschiefer.

there the shales lack copper. The shale thins eastward towards Halle, to almost disappear, and there copper occurs in nodules in the white sand. At all localities, copper content above 1 percent is in the lower 10 to 20 cm of the shale; lead and zinc are principally in the 25 cm above the copper band. Silver accompanies high copper, whereas zinc and copper are antipathic. If Cousins (6) criteria from distribution patterns of multiple metals in a deposit are established, this disharmonic distribution pattern will weigh against a syngenetic origin.

Anomalies to Coincidence of Stratigraphic and Metal Patterns

Pattern of ore distribution within the copper shale conforms to prevalence of reducing reactions; where high oxidation leaves ferric iron in the Zechstein limestone, copper is absent in the area; bleaching or reduction of the ferric

iron in the Red Beds adjacent to the shale is accompanied by deposition of nodules of copper sulphides in the sands. The principal and most continuous deposit is in the highly reducing environment of the black shale. To interject a theoretical consideration, the appearance of increase in Eh value could be due to a raised pH in the vicinity of the limestone although this is hardly consonant with local existence of ferric iron in the limestone itself.

Reconciliation of Patterns

Known metallic mineralization is in the area of the thick Red Beds filling the Rift troughs of Permian age. Known copper mineralization is on the flanks of tectonic swells and independent of the islands and shorelines in existence when the sediments were deposited; generally the mineralized band lies along the zone of the Red Beds. The nonproductive domains in a generally metalliferous zone and the zinc domains are farthest down the flanks of such swells as the Harz Mts. or the Richelsdorf Hills and Thuringerwald. No mineralization is recorded at the ends of the troughs along the Slate Mts. to the westward or along the Ore Mountains to eastward. Erratic discontinuity in mineralization, within the host stratum, is not consonant with currently forming deposits having a sedimentary origin. This ore pattern is the frontal pattern of an artesian circulation but no clue to direction of flow is obvious to me on the basis of the existing data; recharge could be on the flanks of the basin and discharge on the ends, or recharge could be on the ends and discharge on flanks; experimental work suggests that the former is the more probable with the spillway being out towards Hannover (21).

The metallization of the shale, particularly its basal part can be accounted for by derivation of the metals from the red beds through leaching by groundwater circulating under the shale where greatest movement occurs. Local precipitation of copper, lead, zinc and silver can be attributed to the high pH and high reduction potential at the shale horizon. The vanadium is mostly an indigenous component of the shale.

THE CONGO-RHODESIA COPPER BELT

General Features

The Congo-Rhodesia copper belt is a single metallographic province extending from the Bwana M'Kubwa mine to the Zilo Highlands beyond Kolwezi and perhaps even into Angola. The deposits are in three separate zones (Fig. 8); the southern one occupies closely folded synclines inset into the pre-Katanga metamorphosed and crystalline rocks; the central one is along the southern edge of the relatively continuous trough of Katanga system sediments; the northern zone is in the belt of thrust faulting in the Katanga system sediments. Uranium-bearing fissure veins of 600 million years age occur in all belts and, as at Bisbee, Arizona, these veins are earlier than the principal copper mineralization; they are fragmented at N'Kana and Musenoi by the later copper ores. The Roan Antelope ore body represents one extreme

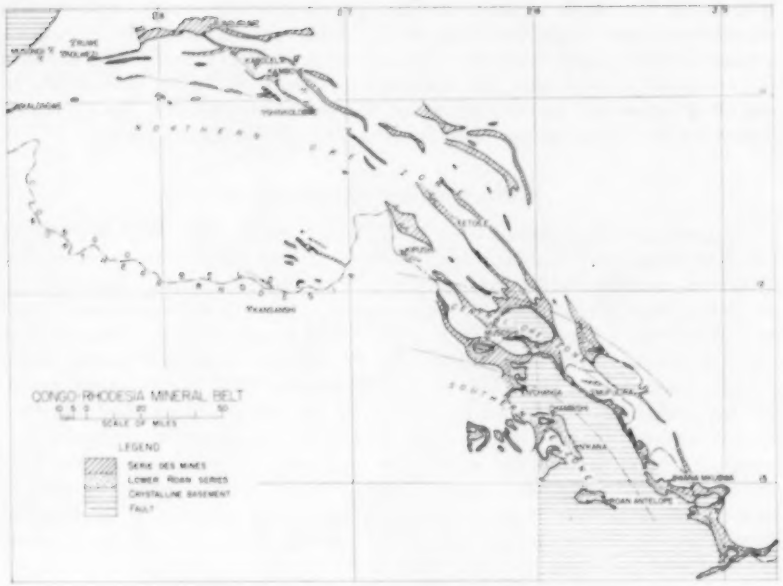


FIG. 8. Geological zones of ore in Rhodesia-Congo border area.

in mineralization just as the Fungurume, Kambove, and Kabolela protores represents the other. Stratigraphic occurrence of ore and succession to major mineralization types over the whole region shows wide departure of ore distribution from age of sediments, sediment facies, and exhibits of systematic change of position in regard to facies. The deposits of the two southern belts have a structural facies in common by having mineralization of ore grade occurring in the vicinity of monadnocks on the pre-Katanga surface; the horizon varies slightly for each district but all are at about the stratigraphic level of the monadnock summits, which rise to nearly the same level from their old surface. The deposits of the northern zone are in breccias located at sharp folds or thrusts in or adjacent to the major thrust plane.

The Stratigraphy in Relation to Ore

The Katanga system rests nonconformably on a crystalline floor; it is well stratified and divisible into the Serie des Mines below and the Kundelungu Series above. Economic mineralization is in the Serie des Mines but metallic minerals occur in the crystallines below and also in structures that cut the Kundelungu Series. Generally the Serie des Mines is divided into the Lower Roan Group, the Upper Roan Group and the Mwashia Group (Fig. 9).

The two southern zones have the ore in the Lower Roan Group of arkose, argillite, siltstone, and quartzite, whereas the primary sulphides of the northern

ore zone are in the Upper Roan Group of limestones and dolomites. This is the first major departure from adherence to a sedimentary facies or even to a stratigraphic zone.

The near coincidence of ore with the favored but different stratigraphic horizon for each of the three structural zones has been an impressive feature. Some mineralization appears throughout the areal distribution of the horizon for the respective structural zones; however, for the central and southern zones, the metal content rises to over half of one per cent only near special structures, namely, buried monadnocks rising on the pre-Katanga System surface whose near uniform summit level controls the pattern to ore distribution at nearly the same stratigraphic horizon (Fig. 10). The ore horizon of the northern zone is a series of bedded dolomites between the siliceous cellular quartzite above and the talcose argillaceous beds below. This member is intensely deformed and erratically fractured and the sulphides are princi-

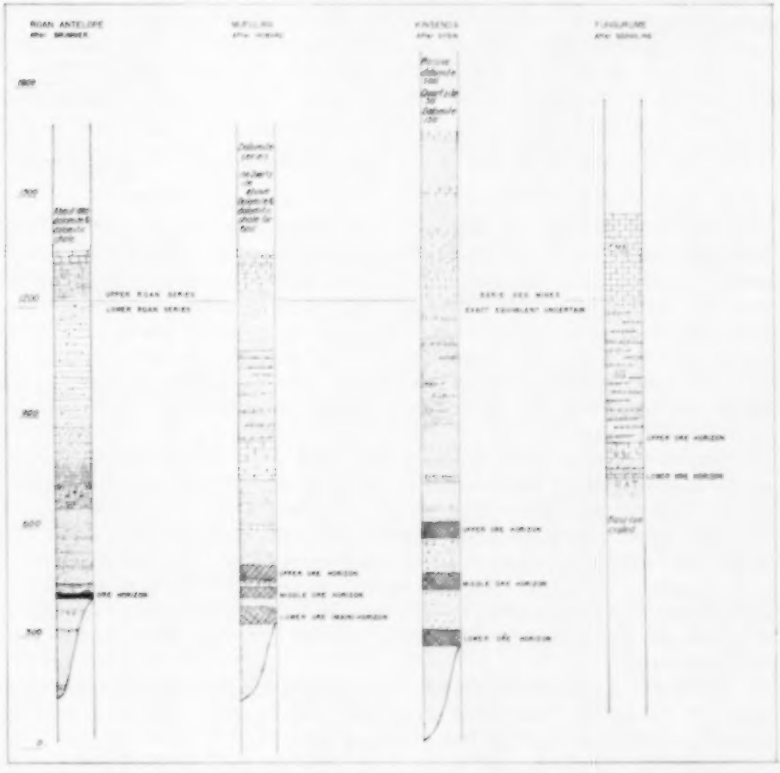


FIG. 9. Stratigraphy of ore zones in the Rhodesia-Congo border area.

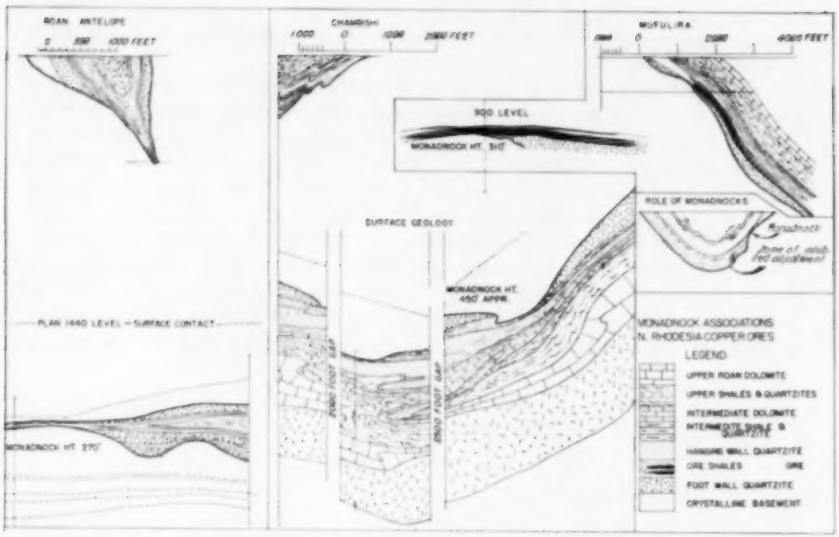


FIG. 10. Relation of Rhodesian ore bodies to monadnocks on pre-Katanga System surface.

pally in veins but appear also as coarse disseminations (26). Within the southern and central zones the Footwall Quartzite of the Lower Roan Group varies considerably in thickness and is absent locally due to irregularity of the floor on which it rests. It is characterized, in all mines by beds up to three feet thick, with pronounced crossbedding such as forms in stream flood plain deposits. Ore is generally above this footwall quartzite, except at N'Changa, and is in a series of argillite, graywacke, or siltstone strata; at Mufulira the upper ore body may be in the hangingwall shale horizon which there is admixed with quartzite.

Mineral Horizons in the Southern Ore Zone.—The base of the ore horizon at the eastern end of Roan Antelope Mine is an intensely sheared rock or gouge 1 to 10 feet thick (Fig. 10 a). Westward the horizon becomes a tremolite schist with dimensional orientation of the tremolite; this basal part of the ore horizon has intense deformation everywhere. A similar tremolite rock occurs at N'Kana. The overlying siltstones in the eastern part of syncline are mineralized down to the gouge and are slightly over 50 feet thick; economic mineralization recedes upward for 30 feet from the tremolite zone in the western area.

Less than one foot of transition separates the hangingwall siltstones from those of the ore horizon which they resemble closely. The rock may be somewhat quartzose but this is not conspicuous.

Locally the "sheared-rock" at the base of the ore zone comes to the surface of the monadnocks on the pre-Katanga surface. Near coincidence of the

ore horizon with the summit of these monadnocks is a recurrent feature, appearing at all mines on this zone, and at Mufulira on the next zone to the north. This suggests structural facies control of mineralization entirely independent of the differing ore horizons at Mufulira.

The appearance of bornite in the most opened up part of an ore host, in an area of prevalent chalcopyrite mineralization, is recorded at Bisbee and Jerome, which are good hypogene deposits. Elsewhere low-temperature chalcocite is a "core mineral" to sulfide copper deposits, bornite is around it and generally earlier, and chalcopyrite and pyrite is a peripheral fringe mineral. This is the zoning recorded in at least the two southern zones of the Congo-Rhodesia mineral belt and seems to be "opening based," rather than "temperature based," or "sediment facies" based.

N'Kana is on the southern zone. A tremolite schist commonly appears above the Footwall Conglomerate at the top of the Footwall grits, here much thicker and more bouldery than usual. (Some boulders are over one foot in diameter and are dispersed as in piedmont outwash.) The tremolite needles are aligned parallel to the glide lines on the folded sediments and locally have been transformed to end up as biotite; much biotite is replaced by chalcopyrite. Granite monadnocks extend well up into the ore horizon; around the monadnocks the Footwall conglomerate increases from 3 feet to 30 feet in thickness and then disappears by overlap; the argillites of the ore horizon become shale partings in a coarse arkose which is highly silicified and indurated.

Rich ore sections are in great drag folds that seem to pile up against the southeast side of the granite monadnocks. Minor drag folds are ruptured and have coarse bornite in vein mineralization as well as the more widespread, fine-textured, disseminated mineralization.

The Chambishi ore horizon is essentially the same zone as at Roan and economic mineralization occurs in the greatly crumpled beds down dip from the intercept with the summit of the granite monadnock (Fig. 10 b). Over extensive outcrops of the ore horizon, no economic ore appears at the surface.

The N'Changa granite monadnock rises above the Footwall Grits at the southeast end of the syncline and comes up to the "biotite schist" band from the Dambo Lode to the New Discovery. The widespread ore horizons are the same as at Roan but others are mineralized also. Near the granite monadnock, the upper shale horizon and the arkose on the monadnock are mineralized. The lower shale horizon has the principal mineralization distant from the monadnock as at the north side of the syncline and also far to the west on the N'Changa extension.

Mineral Horizons on the Central Ore Zone.—The Bwana M'Kubwa, Mufulira, Musoshi, and Kinsenda deposits are on the Central Ore zone. Mufulira will be used as an example (Fig. 10 c). A monadnock of Muva quartzite rises through 300 feet of Footwall Grits to reach the lower ore horizon at the 650 level of the Selkirk shaft where the third or lower ore body and second or intermediate ore body are continuous through 100 feet of feldspathic quartzite up to the Lower Dolomite. Here the bottom of the first or upper ore body comes very close to the intermediate ore body. The

lower ore body is most extensive reaching along the ore horizon for roughly 4,000 feet from the monadnock summit in all lateral directions and down dip. The intermediate and upper horizons are only 60 percent as extensive and are centered over the monadnock summit.

A very considerable part of the copper minerals in the upper and intermediate ore bodies fill fractures and graphitic coatings on the argillite bedding show strong lineation structures. There the distribution pattern to the mineralization coincides with the deformation pattern that centers around the monadnock. Intensity of mineralization in the lower ore body obscures the structure because bornite occurs all through the thoroughly granulated feldspathic grits and arkose.

Generalization Concerning Mineralization.—The occurrence of copper as well as cobalt and silver in amount to be productive at present value is in highly folded Katanga system sediments where these abut on monadnocks rising from the original sedimentation floor. The favored ore horizons are any feldspathic quartzite, siltstone or arkose about level with the monadnock summit. The monadnock material may be any kind of rock but it is generally granite, in places quartzite, or even squeezed conglomerate. Abnormal copper content is in bedding slips, fracture cleavage veins and irregular breccias; this is in addition to some extremely fine grains of disseminated copper sulfides.

The conditions permitting economic mineralization are local "riveting" of the "ore horizon" to the crystalline floor by the monadnocks, which prevents free gliding during similar-folding movements. The ore host was fissured at these sites of uneven strain. The fissuring happens to be nearly but not absolutely at the same stratigraphic horizon because most monadnocks had almost the same summit height. Fissuring provided loci for concentrating flow of the metalliferous solutions. Origin for the solutions is irrelevant; it is important only that the ores are on a pattern of structures of epigenetic origin, are epigenetic, and their continuity will be on a tectonic facies pattern rather than on a sedimentary one.

The Katanga Deposits

The Katanga deposits lie in the third or overthrust zone where klippe commonly contain the mineralization; deposits persisting to relatively great depth are adjacent to the principal or northern thrust plane (Fig. 8). The ore deposits are in the Upper Roan dolomites and their sulphides are in veins and breccias therein; only minor mineralization occurs as a dissemination through the rock (Fig. 11).

These deposits are obviously epigenetic and possess the conspicuous characteristics of those formed in the shallower part of the middle depth zone; in the interest of brevity, detailed discussion of them will be omitted. However the three zones form a part of a system graded towards a shallower depth type as the zones are listed in order towards the Rhodesian platform or craton. In principle the first or Roan-N'Changa zone, the central or Mufulira zone, and many in the third or overthrust zone, are manto deposits;

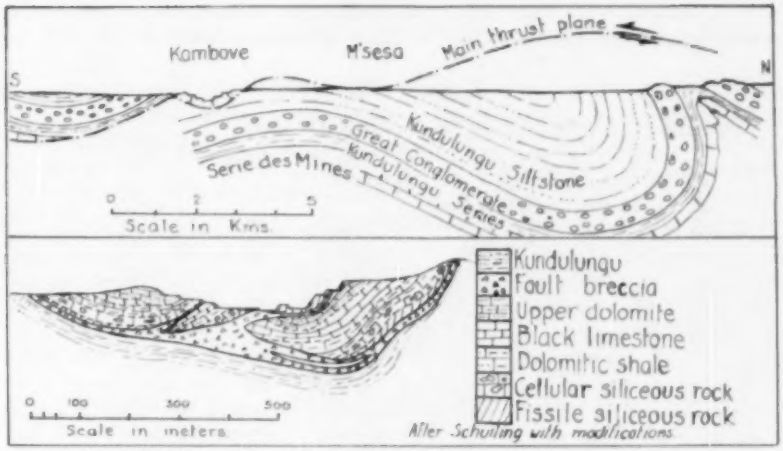


FIG. 11. Occurrence of ore in the brecciated dolomite of the overthrust plate, Kambove, Congo Belge. (After Schuiling) on p. 23 Van Dyk.

however physical failure to produce openings in the host for mineralization—and consequently the favored host—is different from that at Bisbee, Santa Eulalia, or El Potosi. The Katanga deposits do have greater similarity to those of the Chihuahua-Arizona belt.

CONGLOMERATE HOSTS

Turning from the shale-siltstone hosts to conglomerate host rocks, one finds an equally intriguing group of deposits, two of which have been considered already. Deposits in conglomerates show many of the distracting epigenetic structures of the Rhodesian siltstones where pebbles are sliced parallel to the bedding, the ground-water effects seen in the alum shales where the margins of detrital grains are indented by hydrocarbons and sulphides, and introduced columnar ore even with reticulate "vein like" mineral bands resembling hypogene veins. Many features must be accounted for before the relation of pattern to expected continuity of deposits beyond mining development faces can be assessed with any degree of confidence.

THE WITWATERSRAND

The Witwatersrand has produced about one third of the world's gold for half a century, yields a considerable amount of osmiridium, and should be included in the first three uranium areas of the world. Yet origin of its ores has been the basis for one of the most acrimonious debates of our day. Several types of evidence, such as the intense footwall shearing of most productive reefs and the pyrite-thucholite replacement of the quartz pebbles,

will be omitted here, since this topic deals with patterns and the reader is referred elsewhere for summaries on this interesting deposit (10, 19, 23).

Types of Patterns

Patterns of distribution can be considered under:

1. Variation in one metal relative to other metals or minerals.
2. Patterns of anomalous distribution.
3. Areal distribution pattern.

Variation in One Metal Relative to Cumulative Frequency.—Cousins (6) has analyzed the value distribution pattern of economic minerals using cumulative probability curves with special reference to the Witwatersrand gold reefs. He plotted the "Log upper value limit" against the "cumulative frequency" for multiple elements in a deposit using examples of both sedimentary and solution origin and of the Witwatersrand metals. He found that solution deposits had accordant variations for the same metal from various lodes of the same deposit but discordant variations for different metals even from the same part of the same deposit. Detrital sediments gave discordant variation for the same metal from stratum to stratum in the sequence but accordant variation for several metals from various parts of the same stratum. Cousins showed concordance of gold and uranium for any particular reef and concordance of gold with osmiridium and silver over limited areas; however, extension of silver beyond a single mining area introduces departures that are attributable in part to mixing of different reefs into the mill feed particularly for the osmiridium data. Generally the patterns that he has obtained are those of sediments.

The silver content of unrefined gold as determined from mine output on the East Rand between 1921 and 1940 showed a systematic decline from east to west, which could not be attributed to variability in reef source. This variation is in accord with variation in silver content for alluvial gold as it is recovered down-current away from its source.

Patterns to Anomalous Distribution.—Anomalous or apparently erratic distribution of the two principal metals of the Witwatersrand recurs many times and generally where other evidence indicates that volume of groundwater movement was increased. Predictable variation in metal content is in stream channel lines and on unconformities. Examples will serve to illustrate typical departures.

Blyvooruitzicht has an unusual frequency of local columnar gold and thucholite in the base of the Carbon Leader Reef; clearly these are the product of crystallization from solution. The phenomenally rich parts of the reef at the upper levels on the east side of the property are in the "fault trenches" and the "fault ridges" are correspondingly impoverished; this suggests redistribution. Adjacent to some large sills in Maryvale, at the other side of the Rand, the Leader Reef has had almost all gold driven out and highly recrystallized parts of the Reef on Van Dyk are nonauriferous; at other places as on Daggafontein coarse gold appears in some quartz veins.

The above are anomalous cases and they come from areas of solution

movement intensification; however these appear in less than one per cent of the area of Rand reefs; the pattern within the anomalous area is easy to recognize.

Areal Distribution Pattern.—The shoot pattern on the Witwatersrand can be evaluated approximately from the stope pattern on the shareholders mine maps and was so analyzed by Reinecke (24) (Fig. 12). The entire central Rand is mined out as a bed but, where the outcrop and sub-outcrop of the Main Reef Series turns southward both in the Far West Rand and the Far East Rand, broad strips of unpay quartzite separate phenomenally rich shoots. These shoots strike northwestward and most are conglomerate shoe strings with plano-convex cross section; they resemble stream-channel deposits.

The pebbles of the reef conglomerate for any one reef horizon of the Main-Bird Series range to larger size in the east or southeast than they attain in the north or west. (This size variation pattern is reversed for the Kimberley Reefs.) The conglomerates underwent assortment until pebbles touched in the bottom of any reef. Towards the top of a given bed a few pebbles appear and are dispersed in coarse quartz sand. Locally a sorted pebble layer appears in the quartz sand at some distance above the basal pebble zone. The

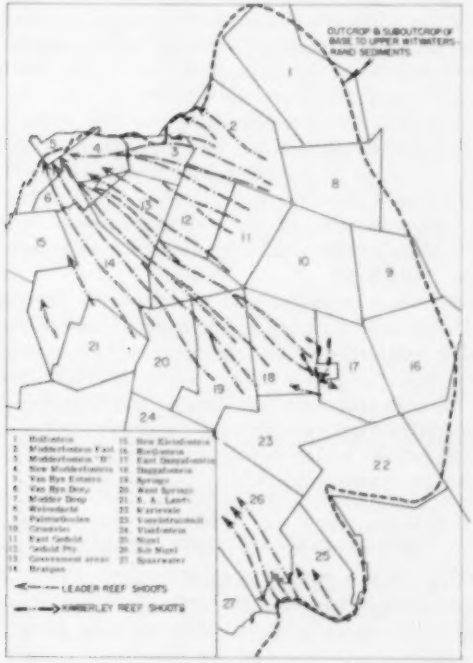


FIG. 12. Generalized shoot pattern on Far East Rand (modified from du Toit).

pattern to vertical distribution for gold and uranium shows that they occur in the lower part of the assorted pebble layers whether these are at the base, middle or almost at the top of a reef.

These areal and vertical distribution patterns for gold and for uranium conform to an alluvial separation of minerals from a great bulk by successive fill and scour of the "light" components in a relatively mature river system. Flow was northwestward during deposition of the Main-Bird Series and southeastward during Kimberley-Elsburg sedimentation. De Kock (9) showed that the values of Ventersdorp contact reef were derived from pre-Ventersdorp outcrops of Witwatersrand reefs by eastward flowing streams; gold appeared abruptly at an intercept and declined in the direction of flow of the stream moving the detritus now making the contact reef.

Generalization

The Main Reef Series conglomerates have an areal pattern to pebble size variation and crossbedded structure, which implies a source to eastward or southeastward. They have the general parallel linear pattern of gravels on a piedmont plain whose length was parallel to the continuously auriferous finer textured conglomerate of the Central Rand. The stream channels were entrenched only slightly into the piedmont surface. The occurrence of pebbles and heavy minerals at the base of assorted pebble layers is the pattern developed by recurrent fill of the channels by unselected detritus followed by scour of the mobile particles from the channel to near the nonconformity surface of the piedmont. Pattern for decline of the silver to gold ratio to northwestward and for distribution of the osmiridium within the lower reefs of the Main Reef Series is in accord with this alluvial origin.

The flow direction was reversed for the Kimberley Reef Series (May Reef). Streams are entrenched deeply at Daggafonstein and are less defined to eastward. Boulders are large at Daggafontein and become relatively fine in the remote Far East Rand.

Minerals have been recrystallized and components reorganized and even redistributed. However the major features of a sedimentation pattern, for particles with high mass relative to area opposed to a current, in both area and vertical distribution and in regard to facies has been maintained and is defined clearly. Search for extensions to ore in either the Main-Bird Reef series or the Kimberley-Elsburg series can be carried out with more realization of anticipated results to testing by visualizing an alluvial pattern than any other concept presented yet.

THE ORANGE FREE STATE GOLDFIELD

The Orange Free State goldfield occupies a basin of Upper Witwatersrand sediments laid in a trough (graben ?) in Lower Witwatersrand strata and older crystallines. The basin is about 30 miles long from north of Odendaalsrust to Virginia and is about 6 miles wide (Fig. 13). More recent faulting has disrupted the continuity of deposits to a degree encountered

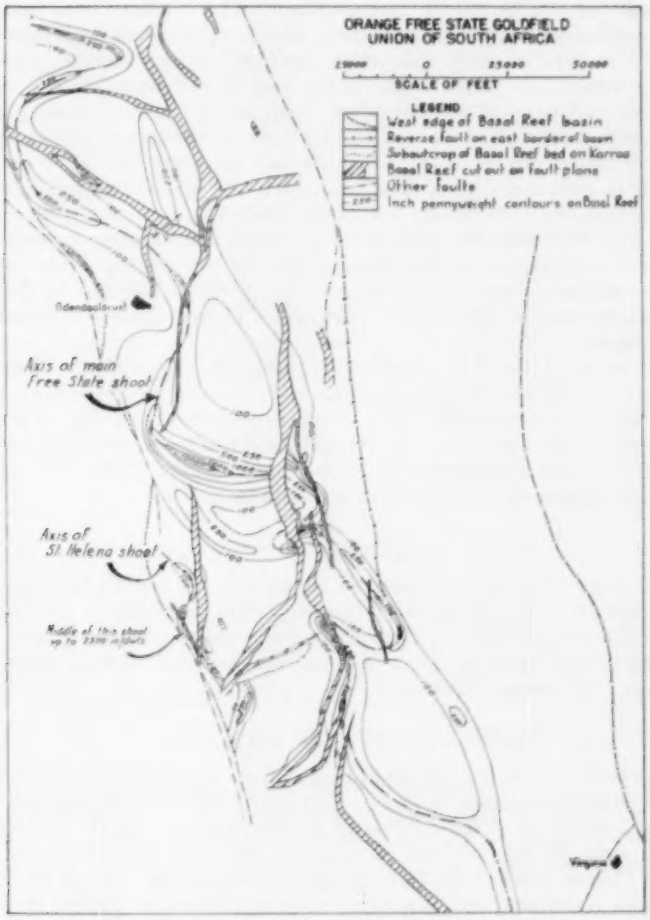

ORANGE FREE STATE GOLDFIELD
UNION OF SOUTH AFRICA
25000 0 25000 50000
SCALE OF FEET
LEGEND
West edge of Basal Reef basin
Reverse fault on east border of basin
Subcrop of Basal Reef bed on Karroo
Basal Reef cut out on fault plane
Other faults
Inch pennyweight contours on Basal Reef
Axis of main Free State shoot
Axis of St. Helena shoot
Middle of this shoot up to 2500 m. faults
Virginia

FIG. 13. Shoot pattern, Orange Free State Goldfield, Union of South Africa.

nowhere else in South Africa. However, restoration of the strata to their undisturbed position appears to show one main gravel deposit meandering down the central valley and one lesser stringer entering at St. Helena.

The pattern to the ore is essentially that of a stream; ore is in a sorted grit in the Basal Reef. Total resources are augmented by the "Subleader" Reef in the Virginia area and the Leader Reef at St. Helena and in the central region. Outlying hills of "footwall" rocks along the "Western Escarpment" of the Basal Reef basin break reef continuity of the reef con-

glomerate or grit in the St. Helena shoot. The northern area near Odendaalsrust has some additional values in thick conglomerates high in the series where a western tributary entered the basin at Van den Heever's Rust farm.

The rich shoots on the south boundary of Geduld Free State, in southern Welkom, and parts of the President Steyn and President Brand mines are just down current, that is southeastward, from meanders. I became interested in this region in 1941 and it has been very stimulating to watch the pattern to gold distribution take form much like a development of a photographic film; by 1947 it was possible to predict pay or unpay values at the Basal Reef level from the Sand River to Odendaalsrust when the pattern was ascribed to assortment in a southward flowing, meandering stream bordered on the east by a ridge extending from just north of Virginia to Bothaville. A highland through the western part of St. Helena made the western wall of the basin.

All splits of the Basal Reef show principal values in the lower part. Values in the Leader Reef are less regular. Gold in the upper reefs appears to be extremely dispersed. This shoot pattern indicates the values to be anticipated in various areas. I feel that the Freddies leases could have been opened up more advantageously by use of this shoot pattern to indicate a different disposition of shafts than was selected.

THE BLIND RIVER URANIUM AREA

The main Blind River occurrence is probably the world's largest uranium occurrence of productive grade. The productive zones are in the lower 200 feet of Mississagi quartzite; a nonproductive uraniferous zone appears within 150 feet of the overlying Bruce conglomerate and also in fault zones which intercept this uranium horizon.

The Principal Pattern

The principal shoot is contained by a sinuous conglomerate zone characterized by stream deposition fabrics and striking northerly from the east end of Luzon Lake at the Pronto Mine to Nordic Lake, along the west side of Quirke Lake to emerge from the Algoma basin in the central part of the Algom Quirke Lake property (Fig. 14). Width of the zone is about 8,000 feet and it is characterized by quartz pebble conglomerates filling a shoe-string lens cut into either pre-Huronian crystallines, or Mississagi basal arkosic conglomerates and siltstones. The pebble assortment in the shoe string indicates that the deposit is a fill and scour strath along a lower Huronian age river flowing north across the incipient Huronian geosyncline (1).

The U_3O_8 content of the quartz conglomerate zone averages about 0.10 percent over about 10 feet thickness for the principal stratum and slightly less for an upper band. The Pronto ore rests directly on the pre-Huronian floor and commonly is extremely thin but has high content; boulders attain 18 inches in diameter here, whereas at Quirke Lake pieces within the ore channel rarely exceed an inch in diameter. Geiger counter scanning of the conglomerate bed at both Algom Quirke Lake and at Pronto show more

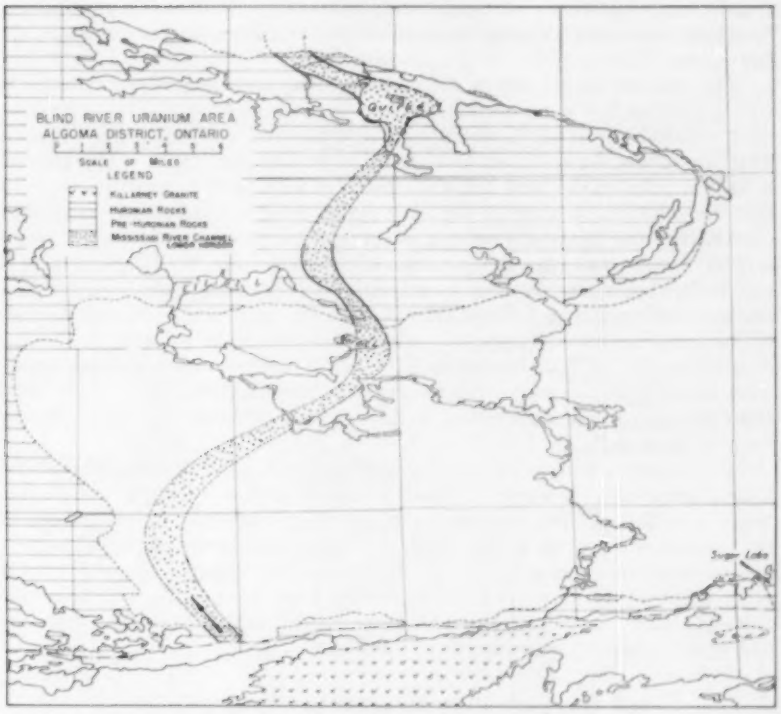


FIG. 14. Uraniferous shoot, Blind River, Ontario.

radioactivity, and presumably more original uranium, at the basal layer of the conglomerate bed. This vertical distribution pattern within the conglomerate shoe string, having rather abundant heavy minerals, conforms to that of a river alluvial rather than to a beach type which has the heavies at the top of the stratum rather than the bottom.

Migration Influences

Near Sugar Lake, north of Massey and about 20 miles east of the Pronto Mine, a thin uraniferous quartz conglomerate occurs in a sericitic band at 150 feet stratigraphically below the Bruce Conglomerate. The band becomes quite thick at Sugar Lake and appears to be fill of a scour channel in the upper Mississagi quartzite. It can be traced for about one mile westward. Radioactivity suggests about 0.02% U.

One transverse fault at Sugar Lake, and another about halfway from there to the Fire Lookout tower, have uraninite mineralization where the fault crosses the Espanola Formation. Radioactivity on the fault ceases after

it passes into quartzites stratigraphically below the uraniferous conglomerate. Uraninite occurs as films on the reddish silicified Espanola formation in the fault zone.

The coextensive pattern of weak radioactivity and conglomerate stands in strong contrast to the intense radioactivity in the fault zones. The faults have their radioactivity fracture-restricted and apparently the radioactive minerals were introduced by solutions and were crystallized therefrom. The absence of radioactivity on the fault below its intercept with the conglomerate suggests that the solutions moving on the fault planes were nonradioactive until they encountered the conglomerate. It is my opinion that the patterns to radioactivity distribution suggest derivation of uranium from the conglomerate; it was redistributed into the fault by migrating solutions particularly where they reacted with the Espanola Formation. The consistently uniform radioactivity in the conglomerate is compatible with a detrital origin whereas the erratic distribution in the fault conforms to selective crystallization around nuclei. This is an instance where migration and recrystallization has made local concentrations much higher than in parent rock without the metals coming from a "magma."

The Sugar Lake type of occurrence recurs within the Webbwood Area on Lake Agnew and elsewhere. These examples serve to highlight the characteristics of deposits from solution and contrast them with the persistence of the conglomerate occurrences. Patterns of uranium ore in the conglomerate are sedimentation facies linked; in the absence of strong evidence for some other origin of the patterns as well as a full exposition of physical principles that will yield those patterns, one is permitted to presume that both ore and host are detrital sediments.

THE COLORADO RIVER PLATEAUX URANIUM DEPOSITS

The Colorado River Plateaux area includes a great region drained by the Colorado River and underlain by either nearly horizontal or gently folded strata. It has two great uranium producing stratigraphic horizons; the oldest occurs on the unconformity surface developed during the middle Triassic epoch, often called the Shinarump conglomerate but varying in time equivalent with the locality; the youngest is the Salt Wash member of the Morrison Formation. The geographic disposition of ore pattern features for the two horizons do not coincide even although they have a number of physical features in common (Figs. 15, 16).

Characteristics of Productive Deposits

The features that are common to all productive deposits include:

1. Occurrence is either in or immediately adjacent to a "shoe-string" sand or conglomerate representing a river channel (Figs. 17, 18).
2. The ore carrying member—channel conglomerate or sand, or sand and shale adjacent to a channel—contains more than 20 percent of –325 mesh detritus.

3. Every channel occurrence with significant associated uranium carries reddish-brown jasperoid pebbles or sand grains containing fossils of the Word Stage (Permian) and having as much as 0.05 percent of uranium in specimens analyzed.

The converse of these unvarying associations is valid for all sediments of the "Plateau area" that I have visited, if the associations are considered in

FIG. 15. Uranium shoot pattern in "Shinarump" horizon of Colorado River Plateaux.

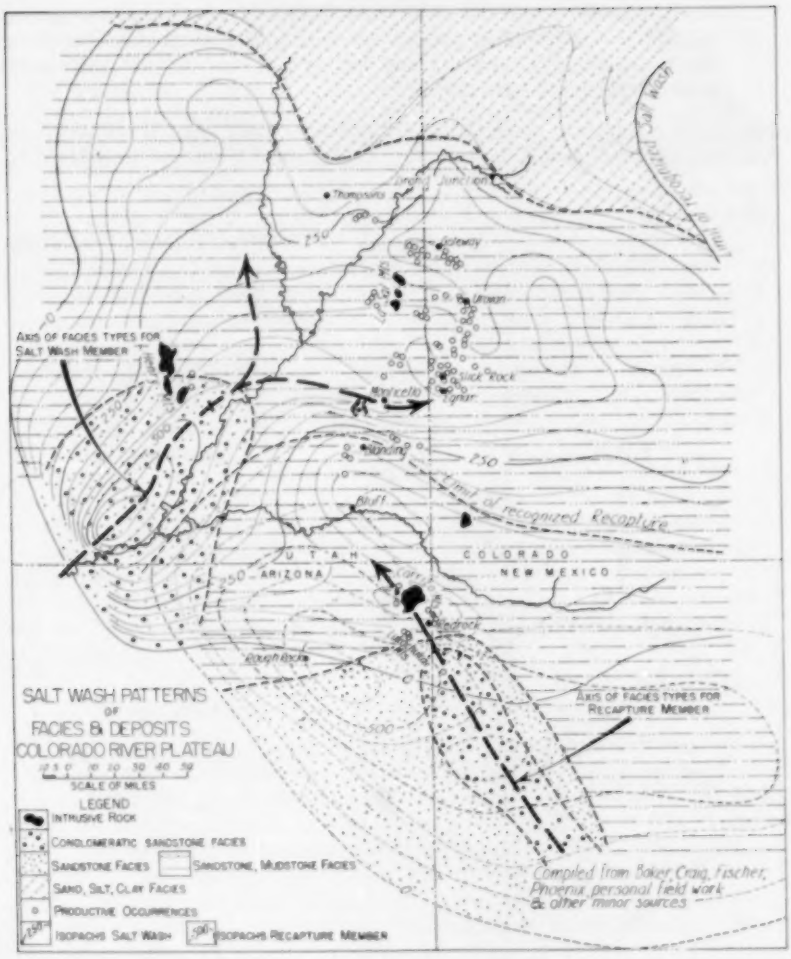


FIG. 16. Uranium deposit area of Salt Wash strata in Colorado River Plateaux.

order beginning with the first; the second is valid only if applied to a site embodying the first requirement and the third is applicable only if it occurs in conjunction with the first two. The following instances illustrate these features.

Shoe String Channels.—The principal wartime producers from Salt Wash beds in Long Park were under and lateral to shoe-string sands with plano-convex cross section; Monument No. 1 and Monument No. 2 Mines in the

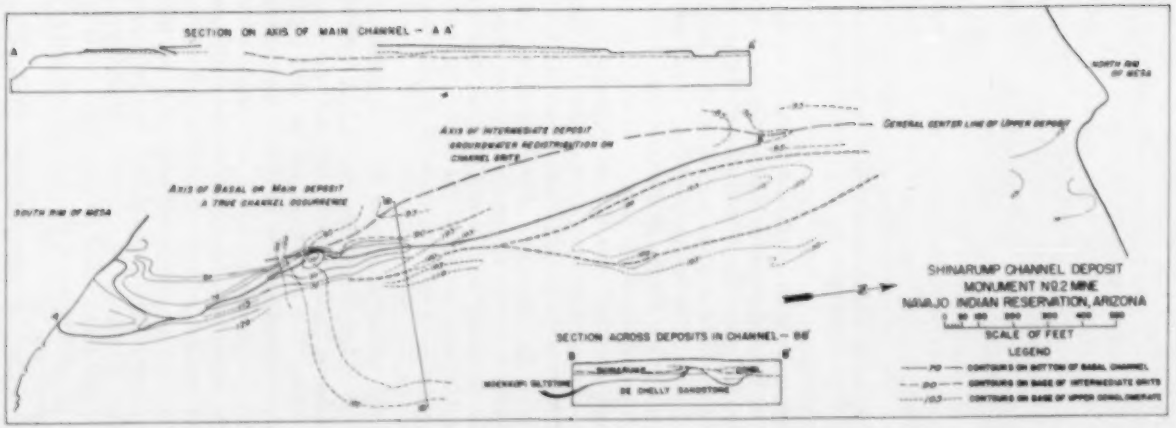


FIG. 17. Monument No. 2. Shinarump channel deposit, Monument Valley, Arizona.

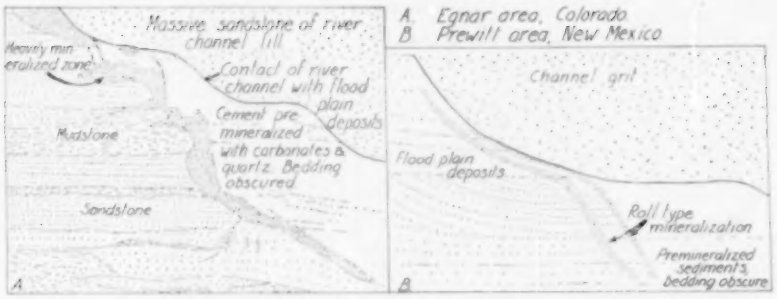


FIG. 18. Mineralization in dilation zones along river channel sands in the Salt Wash member of the Morrison formation.

Shinarump conglomerate were in northwest trending shoe-string conglomerates that represented channel deposits from northwest flowing streams.

Low Permeability of Host.—The Salt Wash beds lateral to a shoe string, itself usually unproductive, had over 40 percent of shale in lenticles between relatively thin sand layers. The mineralized Salt Wash interbedded sands, clays and bentonites are below the top of the associated shoe string and have the uranium minerals principally either in the thin sands or along transverse dilation cracks through sand and clay and terminated at the under surface of the shoe string. The most intense mineralization is along the dilation crack and constitutes most of the so-called rolls; other bands of mineralization commonly are parallel to the main one. Principal amount of mineralization as distinct from intensity is in waning amount outward along the sand beds and is confined by the bounding shale lenticles. Only thin films of carnotite lie along bedding slip planes in the clay. The role of the clay lenticles seems to be to reduce dispersion of the uranium from the dilation crack that seemed to provide access.

Both Monument No. 1 and Monument No. 2 uraniferous conglomerates had over 20 percent of –325 detritus intimately mixed with the pebbles and sand. A channel deposit north of Cane Valley and nearly midway between the two Monument Mines had only 5 percent of –325 mesh detritus and, although copper stained and radioactive, carried inconsequential uranium.

The Monument No. 2 deposit has uranium and vanadium ores in the upper permeable grits of the Shinarump horizon from the north end of the mine for about two thirds of the distance to the south rim of the principal mesa (2). Prevalence of this ore type declines southward or down pitch; the frontal uranium distribution pattern in the beds and the radioactive equilibrium suggest that the deposit is uranium in migration; by contrast most uranium of the mine is in the impermeable basal conglomerate and is principally in or immediately adjacent to scour basins in the channel and appears fixed in place at least until the miners get at it.

Jasperoid Detritus.—The shoe string sand of the Maggie S. Mine in Long Park, to mention a specific place, had numerous worn grains of a reddish

chalcedonic quartz (jasperoid); about 20 percent of the pebbles in Monument No. 1 and No. 2 are either smoky quartz or fossiliferous jasperoid. The Cane Valley occurrence was located by airborne radiometric surveys but close spaced drilling failed to disclose a productive body; the channel conglomerate has jasper and jasperoid pebbles; however, the occurrence has less than 20 percent –325 mesh detritus and so does not meet the second requirement. The radioactivity indicates that uranium was present but the impermeability requirement (2) was not met; the copper minerals are oxidized and the logical inference is that uranium is not present because the rock was permeable enough for solutions to penetrate freely and remove the uranium. A similar condition has been noted for the Monument No. 2 channel on the hogback to northward from the productive part.

Generalization.—Permeability in a formation is the most serious deterrent to expectation of uranium. This is as true of a structure or a horizon or a formation as it is of a facies—like a channel—in a formation. The permeable Wingate, Navajo and Entrada sandstones constituting almost two thirds of the stratigraphic column for the productive region have inconsequential production and the slightly less permeable Kayenta sandstone is little better (Fig. 19). The Entrada sandstone carries vanadium ore, with some uranium, only in the eastern part of the area where it has either silt or "hydrocarbons." Many channels at Temple Mt. striking S 22° E and some near the crest of the San Rafael Swell, have less than 10 percent of –325 mesh detritus but, where they are uraniferous, the openings are closed by old high-index bituminous substance and other younger "hydrocarbons."

The Areal Pattern on the Upper Triassic Unconformity

The Shinarump and associated conglomerates of Chinle Age rest on Moenkopi sandstone and shale throughout the basins of the San Juan and Dolores Rivers east of the Colorado and the Fremont and Escalante Rivers to westward from it. This Shinarump Basin had streams draining into it from the south, east and north and flowing out westward through the Kaiparowits Region. The conglomerates on the unconformity southward from Lukachukai Trading Post (Arizona), west of Blanding (Utah) and at Gateway (Col.) have Chinle age and are on the productive fringe of the basin for some distance downstream; fine silt was deposited with the pebbles in the flood deposits.

The conglomerates contain rocks and minerals such as Word Age jasperoid, terminated zircon crystals, smoky quartz and others that indicate exposure of formations, including crystalline types, even older than those on which the upper Triassic age conglomerates rest. This highland rim persisted in the Uncompahgre, Elk Mts. and locally in the Ft. Defiance area until the Entrada overlap.

The Shinarump streams attained assortment of their detritus up current from the central part of the basin that extended from the San Juan River to the town of Escalante and perhaps as far as the Circle Cliffs area (Fig. 15).

FIG. 19. Stratigraphic distribution of uranium deposits, Colorado River Plateaux.

This domain of assorted Shinarump has uranium occurrences but not in presently productive amounts.

A mule-shoe-shaped area lies between the two limiting nonproductive domains and includes the occurrences of the San Rafael Swell, Moab, White Canyon and Monument Valley. This pattern coincides with a specific conglomerate facies of upper Triassic age which possesses low permeability.

The pattern is very blurred locally. Solutions have moved the uranium,

thousands of feet in some instances, but have generally kept it in the host rock facies; only rarely, as in the Temple Mt. collapse structure, have they caused dispersion comparable to that in the Sugar Lake occurrence of the Blind River area. The nature of the solutions gave a moderate reduction potential and near neutral pH. The frontal patterns suggest that they were artesian but origin is immaterial to search for ore. The discovered occurrences are in river channels in a near headwaters part of the upper Triassic drainage system.

The Areal Pattern of the Salt Wash Deposits

The Salt Wash member of the Morrison Formation was deposited as two overlapping fans by two streams; the major stream emerged into the Plateau area at about Lees Ferry; the minor stream came in through the Farmington Basin. The latter was the dominant influence northward to the Carrizo Mts. whereas the former dominated the remainder of the Colorado River Plateau where Salt Wash beds are found. The deposits have two distinct facies; the first is a highly assorted river channel deposit with a natural levee facies border; the second is a flood plain deposit with flood sandstones and desiccation mudstones. The river channel facies changes from conglomerate in the southern Henry Mts. to grits at Blanding and fine sands in the Long Park area.

Considerable production has come from widely scattered parts of the Salt Wash but the major output has been from those flood plain deposits flanking shoe string channels with sand size detritus, and found extending in an arc from Green River (Utah), southeast past Thompsons to Long Park, Egnar and Slick Rock on the Lees Ferry system and from Rough Rock through the Northern Lukachukai Mts. and Carrizo Mts. on the Farmington Basin system (Fig. 16).

The Salt Wash pattern is discordant geographically with the Shinarump pattern but matches a geologic facies pattern of its own. Most Salt Wash uranium is in and along dilation cracks imposed on the flood plain sediments by the relatively porous massive shoe-string channel jasperoid bearing-sand behaving as a platten. The uranium and vanadium minerals are crystallized in and along dilation cracks, which terminate against the underside of the shoe string. The pattern indicates that they emanated from the shoe string and are retained locally as withdrawn in solution to impermeable hosts where they appear in sand in waning amounts away from the dilation cracks.

I feel that students of the Colorado River Plateau have been distracted by the solution phenomena and deposits around the microscopic grains and have extrapolated from them to one possible origin without systematically fitting together increasingly larger items of the pattern. Solutions have played a great part in locating Salt Wash uranium most of which is no more at the original site than it is at Cane Valley, but the components on which the solutions worked had a sedimentation pattern; this they modified little more than solutions working on the Witwatersrand conglomerates. The ore textures and fabrics such as cuspate indentation and replacement of the pebbles

and of sand grains, by everything from the thucholite-like hydrocarbons to roscoellite and tyuyamunite, and veining of the sediments by ore minerals, have not been distinguished yet from the solution features in the mineralized parts of the Kupferschiefer and the Swedish alum shales. These are the inevitable acts of ubiquitous groundwater, which seems to have been rather uninhibited by human opinion concerning its behavior.

CRITERIA FOR CONTEMPORARY EMPLACEMENT

Identification of either host rock or tectonic structures as the feature that is contemporary with mineral emplacement is fundamental to estimating trend to a deposit in advance of mining and even for assessing the extension to mineralization beyond mine workings. Often this assessment must be done on small areas or even specimens the size of drill cores. Generally all evidence must be weighted and the sum of all the parts considered in order to decide whether the metals were emplaced with the grains of the sediment and crystals of igneous rock before either became capable of transmitting stress in the direction it was received or whether they are contemporary to tectonic structures imposed on rock. The former are truly syngenetic; the latter are strictly epigenetic; between the two are a whole range of problematical cases characterized by varying degrees of redistribution of original sedimentary, or even hydrothermal igneous components. Deposits by redistribution include as broad types, first, ores redistributed within the original host and including most chromitites, asbestos, and Adirondack nontitaniferous magnetite; second, ores redistributed beyond the original host but near it and including the Sudbury nickel ores in the definitely hot category, and the Salt Wash uranium ore in the atmospheric temperature category.

MINERALIZATION CONTEMPORARY WITH ROCK COMPONENT ORIGIN

Metallic minerals contemporary with host rocks will have their distribution pattern consonant with the pattern of the host. These patterns may be expressed in areal distribution, vertical distribution, or paragenetic distribution.

Areal Distribution.—Hosts aggregated by swiftly moving water will have the mineral concentration along the axis of principal flow (river alluvials). Hosts aggregated by sulphide-producing bacteria have the mineral concentration in the center of basins away from inflow of oxygenated water (Swedish shales). Silicate magma hosts have principal metal concentrations excluded to the last part to crystallize, generally towards the upper part of the intrusive and interstitial to the principal pyrogenic minerals (Nizhne Tagil platinum). Each has a symmetry of areal pattern relative to the host facies, which is not disturbed seriously by later redistribution.

Vertical Distribution.—Moving water leaves the high "inertia" particles at sites of great rate of change in water velocity. Depth-velocity studies of stream flow show that this occurs at the river bed during time of scour. On a beach the rate of change is greatest at the wave uprush line. The first type has the heavy minerals move downward and appear at the bottom of an

assorted series; the latter has the heavy minerals move upward and appear at the top of an assorted series.

The top of thick tabular intrusives is the last part to crystallize and heavy residues of magnetite, ilmenite, and coulsonite are excluded to this upper fraction in the Bushveld and the great anorthosite masses.

Paragenic Distribution.—Detrital grains of metallic minerals have higher specific gravity than their assorted hosts and they settle, with the later fine filler, into the interstices to give the semblance of later minerals; also they are generally very refractory and, in the process of cementation, some solution of the host induces indentation of its surface by the refractories.

Concentration by silicate exclusion places the metallic minerals as anhedral grains between nearly euhedral pyrogenic silicates; reaction products between pyrogenic and metallic minerals are inconsequential. As in the instance of the detrital minerals, concentrations near economic amounts are in the interstices.

MINERALIZATION CONTEMPORARY WITH TECTONIC STRUCTURES

Mineralization contemporary with tectonic structures is solution emplaced and has its distribution pattern affected both by chemical responsiveness of the host and also by provision of solution passages. Chemical responsiveness may be rock facies influenced and give a pattern suggestive of deposition contemporary with rock aggregation; however solution passages are tectonic guided and these furnish the critical indices for occurrence within the host facies in most cases. Mineral record of solution access ways and their effect, may be considered in regard to areal distribution, vertical distribution and paragenetic distribution.

Areal Distribution.—Many deposits are distributed in or along transcurrent fractures through all rocks up to an unconformity; these are contemporaries of the tectonic structures rather than of the host rock. Dissension begins where host fractures are absent or discontinuous short of an unconformity as in the Salt Wash carnotite occurrences, Witwatersrand reefs and the Calumet and Hecla conglomerate.

Immigrant solutions give asymmetry of metallic mineralization relative to axes of the host facies even in hydrothermal rock, such as quartz veins like that in the Central Eureka Mine (18), conglomerate such as the Calumet and Hecla deposit, and igneous rocks such as the Kearsage amygdaloid. Asymmetry of mineralization is not obvious lateral to and under the shoe string sands of the Salt Wash beds and the fractures followed by the rolls do not go through the shoe strings; these pattern features are not consonant with deposits formed by immigrant solutions and are not so regarded.

Generally for any single mineral deposit, or vein system forming a deposit, the lowest temperature and latest minerals form a core within the region of greatest fracturing or opening of the host to solution. This is a centered pattern with centripetal zoning. In the instance of hypogene epigenetic ores these core minerals are the least oxidized in a series; for supergene redistributed ores they are the most oxidized or hydrated in the series.

Vertical Distribution.—No consistent variation in intensity of mineralization by immigrant solutions relative to depth is obvious. However, where access paths have been identified at Calumet and Hecla (5), Tintic (3), Jerome, Central Eureka in California (18), and Blyklippen (13), metallization has been most intense on the host approach side; this is equally valid for supergene, hypogene and frontal sources for solutions.

Paragenetic Distribution.—Immigrant metallization occupies secondary fractures of either megascopic size, or microscopic size at high frequency of occurrence, where deposits are contemporary with tectonic features. As pointed out under areal distribution, the sequence to appearance of the solution emplanted minerals is in order of increasing states of reduction. This order is changed little where emplantment is by supergene solutions from where it is by hypogene types.

In those instances, where solutions merely redistributed local elements, over-all reduction or oxidation changes are inconsequential.

AMHERST, MASS.,
September 24, 1959

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GEOCHEMICAL PROSPECTING AND APPRAISAL OF NIOBIUM-BEARING CARBONATITES BY X-RAY METHODS

L. VAN WAMBEKE

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ABSTRACT

The main source of niobium at present is in granites and granitic pegmatites, and in alluvial or eluvial deposits derived from them. The future production of niobium probably will be primarily from carbonatite deposits.

A mineralogical and geochemical study of carbonatite samples from Lueshe, Kivu, Belgian Congo, by the combined X-ray diffraction-fluorescence method indicates that niobium is distributed in pyrochlore, pyroxene, and zircon. Strontium is also characteristic of these carbonatites.

The geochemical association of niobium and strontium as well as a high Nb/Ta ratio can be used in alkaline petrographic provinces as the basis of preliminary geochemical prospecting for niobium in carbonatites, their covering soils and the associated superficial manganese-iron ores. Rapid and semi-quantitative determination of niobium, strontium, barium rare earths, zirconium and titanium in mineral samples can be made by X-ray fluorescence. For a detailed geochemical prospecting and for the appraisal of niobium-bearing carbonatites two direct methods of X-ray fluorescence analysis have been developed. For rapid estimation of the niobium content both direct methods have an accuracy of less than 12 percent and a sensitivity of 5 to 20 ppm of niobium. Between 100 and 200 analyses can be made per day and per man. The only disadvantage of this method is that the measurements must be made in the laboratory.

Field measurements of radioactivity, paper chromatographic analyses used in conjunction with X-ray fluorescence determinations were used in discovering a niobium-bearing carbonatite in Kivu, Belgian Congo.

INTRODUCTION

THE ore minerals of niobium and tantalum are members of the columbite-tantalite and the pyrochlore-microlite-betafite[1] series. *Columbite-tantalite* containing more Nb than Ta is found in potash-rich pegmatites especially in the quartz-perthite-plagioclase-muscovite zone and may be associated with radioactive yttrium-rich niobotantalates such as euxenite and samarskite. Columbite-tantalite with a lower ratio of Nb to Ta is present in some soda-lithia pegmatites principally in cleavelandite-quartz-spodumene zone or less commonly in replacement bodies of the same composition (1, 2, 3).

Some granites contain enough columbite-tantalite for profitable exploitation as, for example, some of the Younger granites of Nigeria (4, 5). Because of the depth of the granite intrusions, the pegmatite stage is represented mostly by deuteric alterations. These columbite-rich granites and also the associated pyrochlore-bearing porphyritic granites, can be compared to the porphyry copper deposits in which hydrothermal alteration is important (6, 7).

Alluvial and coastal deposits are the present source of niobium and tantalum. They are formed principally in tropical and equatorial countries such as Australia, Belgian Congo, Brazil, India, and Nigeria, where weathering is rapid and extends to considerable depths. The chief minerals columbite-tantalite, more rarely pyrochlore or microlite are associated with magnetite, monazite, rutile and other minerals in the black sands. The original source of the niobium and the tantalum in these alluvial and coastal deposits are the pegmatites and the granite intrusions and in places carbonatites (for Nb).

The partition of the minerals belonging to the *pyrochlore-microlite-betafite* series is controlled mainly by the geochemistry of the crystallizing magma or fluids. The niobium members of this series are found in granites, nepheline syenites, and their pegmatites and in carbonatites, whereas the tantalum members occur only in granite pegmatites. Pyrochlore and betafite are especially common in the biotite-rich part of quartz-perthite-plagioclase zones of granitic pegmatites but are rare in the soda-lithia pegmatites. In potash-rich pegmatites, radioactive pyrochlore and betafite are associated with calcic plagioclases and titanium and rare earth minerals such as allanite, aeschynite and priorite.

The niobium in granites may be as much as 20 to 30 ppm and is commonly more abundant in pegmatites, but a higher concentration—100 to 300 ppm—is found in the alkaline igneous rocks and their pegmatites and veins (8, 9, 10). In nepheline syenites and their pegmatites, the niobium is mainly in pyrochlore with lesser amounts in the titanium minerals, perovskite, loparite, fersmannite and in the zirconium minerals, eucolite, eudyalite, polymignite. The carbonatites derived from alkalic magmas contain between 100 and 7,000 ppm of niobium. The carbonatites, like the genetically associated igneous rocks are

[1] From our mineralogical study, betafite can be considered as the titanium members of this series (see also Satterly, 36).

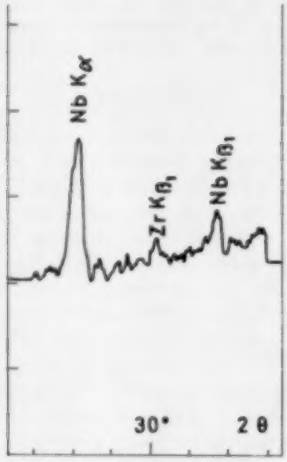


FIG. 1. Presence of niobium and zirconium in aegyrite from the niobium-bearing carbonatite of Lueshe, Kivu, Belgian Congo.

characterized by a marked impoverishment in tantalum as compared to the more acid igneous rocks and pegmatites.

MINERALOGY AND GEOCHEMISTRY OF THE LUESHE DEPOSIT—KIVU, BELGIAN CONGO

The mineralogy of carbonatites has been treated by many authors in the literature (11, 12, 13). Carbonatites occur in the alkalic and subsilicic petrographic provinces and are genetically associated with melanocratic rocks such as dunites and micaceous pyroxenites or with leucocratic rocks such as nepheline syenites. The mineralogical classification of Pecora into simple and complex types stresses the economical importance of both types of carbonatites. The simple carbonatite of Lueshe, Kivu occurs in the graben area where several nepheline syenite intrusions and also complex carbonatites (41, 45, 37) are known.

De Bethune (41) has described briefly the Lueshe carbonatite the first pyrochlore-bearing carbonatite discovered in Belgian Congo. The mineralogy and the geochemistry of samples of this deposit were studied by the combined-diffraction-fluorescence method described previously (42) some samples contain rhombohedral calcite (94% by weight), aegyrite (4.3%), pyrrhotite (1.1%), apatite (0.3%), and pyrochlore (0.3%); other feldspars, zircon, manganiferous carbonates and dolomite.[2] The calcite has 7,440 ppm of Sr

[2] A new niobium mineral Lueshite ($NaNbO_3$) isomorphous with perovskite ($CaTiO_3$) was recently found in this deposit and will be described by Safiannikoff in the Société Belge de Géologie (personal communication).

and 280 ppm of Ba that substitute for Ca in the lattice. The titaniferous aegyrite contains 5,000 ppm of Mn, 300 to 400 ppm of Zr, 780 ppm of Nb_2O_5 and traces of Sr. The presence of niobium in the crystal structure of aegyrite has not been previously described. Figure 1 gives the spectra for pure aegyrite hand picked from a magnetic concentrate.

The presence of niobium in the pyroxene structure is explained by the closeness of ionic radii of Ti^{4+} (0.69 kX) and Ti^{3+} (0.69 kX) with Nb^{5+} (0.69 kX) and also by the possible replacement of (Ca Ti) by (Na Nb). Like calcite, apatite contains between 4,000 and 6,000 ppm of Sr but has only 43 ppm of Ba. Zircon from Lueshe contains ceric rare earths and between 100 and 300 ppm of Nb_2O_5.

GEOCHEMICAL CHARACTER OF CARBONATITE PYROCHLORES

X-ray fluorescence analysis was used to distinguish rapidly between pyrochlores of different origins. Pyrochlores with a high strontium content and a high Nb/Ta ratio are typical of carbonatite deposits. The strontium content in carbonatite pyrochlores varies from 1,000 to 8,000 ppm, whereas pyrochlores from granites or granitic pegmatites show only a small content of strontium ranging between 10 and a maximum of 450 ppm. Pyrochlores from nepheline syenites and their pegmatites have generally an intermediate amount of strontium. The distribution of niobium, tantalum, strontium and in some cases barium in pyrochlores follows the geochemistry of the parent igneous rocks and can be used for the prospecting of carbonatites because strontian pyrochlores are commonly found in alluvial or eluvial deposits. Figures 2 and 3 show part of two X-ray spectra taken on two radioactive pyrochlores from the carbonatites of Lueshe and Mbeya where abnormal amounts of strontium were observed.

GEOCHEMICAL PROSPECTING OF NIOBIUM-BEARING CARBONATITES

In order to arrive at some principles of geochemical prospecting applicable in general to niobium-bearing carbonatites, a study by means of X-ray spectrometry was made on samples of carbonatites, soils, placers, and superficial manganese-iron ores from Lueshe (Belgian Congo), Barreiro (Brazil), Kaiserstuhl (Germany) and from a new deposit in Kivu, Belgian Congo. As a result of this study it would appear that the prospecting for niobium can be divided in two main stages:

1) *Preliminary or strategic prospecting* to find a primary or secondary anomaly that may correspond to a niobium-bearing carbonatite. This may be accomplished together with a radiometric and a geochemical prospecting based on a semiquantitative determination of the geochemical criteria characterizing niobium-bearing carbonatites.

2) *Detailed geochemical prospecting* to outline the intensity of the anomaly by more careful niobium analysis of the soils.

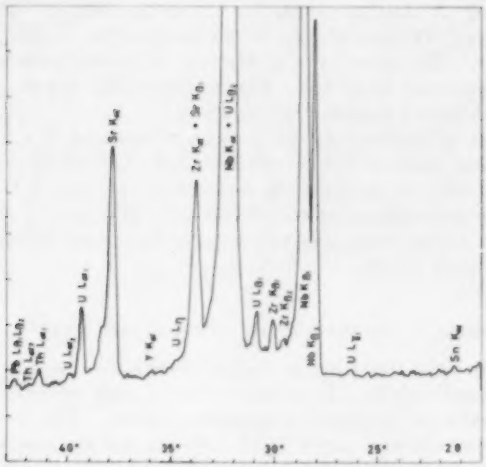


Fig 2

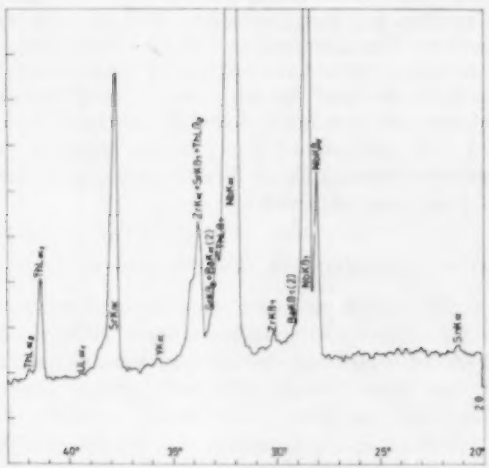


Fig 3

FIG. 2. Typical radioactive pyrochlore of niobium-bearing carbonatite showing an abnormal amount of strontium (Lueshe, Kivu).

FIG. 3. Typical radioactive pyrochlore of niobium-bearing carbonatite showing an abnormal amount of strontium and barium (Mbeya, Tanganika).

Preliminary Prospecting

The detection of niobium-bearing carbonatites can be done in several ways, but the principles of the preliminary prospecting are based on geo-

logical, geochemical, and mineralogical concepts. As the niobium-bearing carbonatites are genetically associated with alkaline magmas, the preliminary prospecting can be limited to petrographic provinces characterized either by melanocratic or by leucocratic alkaline igneous rocks. Such petrographic provinces are known in Central Africa around all the graben areas, in the Mesozoic province of Southeast Brazil, and in many other countries of the world. The graben area and its border in the Belgian Congo is a very favorable area because there are both nepheline syenite intrusions, simple carbonatites (Lueshe), and complex carbonatites (Karonge, Urundi). This area was picked therefore for the application of some geochemical criteria described below, and for field examination, and a new niobium-bearing carbonatite was discovered in Kivu.

Radiometric Prospecting.—Carbonatites commonly can be distinguished from other carbonate rocks by their radioactivity because they contain uranium and thorium and commonly both elements together with their disintegration products. The radioactive elements are in accessory minerals such as pyrochlore, monazite, thorite, uranothorianite, zircon and apatite that concentrate in residual or eluvial soils. Radioactive prospecting was successfully applied to the discovery of some niobium-bearing carbonatites deposits particularly in the Lake Nipissing area, Canada (20) where abnormal radioactivity was detected in outcrops. Abnormal radioactivity was recorded with a portable scintillometer in the soils and the superficial manganese-iron ores above the new carbonatite deposit in Kivu and the low uranium and thorium content was confirmed by X-ray fluorescence analyses. The low radioactivity of some carbonatite deposits, for instance Lueshe, makes a scintillometer the most appropriate detector.

Preliminary Geochemical Prospecting.—a) *Analysis of carbonate rocks.* It is often very difficult for a field geologist, especially in tropical climate, where rocks are deeply weathered to distinguish outcrops of carbonatites, metamorphic or sedimentary carbonate rocks. This distinction can be established rapidly by the use of the simple geochemical criteria summarized below:

1.—Carbonatites have a high niobium content ranging from 100 to more than 10,000 ppm and also a high Nb/Ta ratio from 30 to more than 300 (8, 9, 11). With few exceptions (see below) niobium is practically absent in metamorphic and sedimentary carbonate rocks.

2.—Carbonatites are characterized by a notable enrichment in strontium. The values reported by Higazy (43), Russell (44) and Pecora (11) confirmed by our measurements range between 2,500 and 7,750 ppm of strontium. The average content of strontium in sedimentary and metamorphic rocks is only 640 ppm (Turekian and Kulp, 46) and is thus below the lowest values of carbonatites. Some carbonate veins are, however, rich in strontium but do not contain niobium.

3.—Carbonatites can be distinguished in most cases from other carbonate rocks by the presence of uranium or thorium or both elements.

4.—An enrichment in rare earths especially the ceric group is characteristic of carbonatites. The content in rare earths ranges from 100 to more

than 4,000 ppm in carbonatites. In sedimentary rocks, it does not exceed several 10 ppm. At Mount Chilwa, Smith (26) reports 1,000 to more than 4,000 ppm of cerium and lanthanum for some samples of carbonatites.

5.—Zirconium and titanium are also enriched in carbonatites but data are lacking on the distribution of both elements in the other carbonate rocks. Probably, these two elements permit also a distinction between carbonatites and other carbonate rocks.

6.—Enrichment in barium and phosphorus is also noted in carbonatites but these elements are not so characteristic to permit a sharp distinction between carbonatites and carbonate rocks.

In some cases, alkaline igneous rocks can lead to pyrometasomatic ore deposits in limestone (for instance, Barreiro, Brazil). These ore bodies become then enriched in some mineralizing elements such as Nb, Sr, P, Ba, rare earths, Ti, Zr and therefore their geochemistry is very similar to that of carbonatites (25). On the basis of the geochemical distribution, a sharp distinction between carbonatites and other carbonate rocks can be easily established by semi-quantitative analyses done on a few samples of rocks. The more characteristic geochemical elements found are Nb and Sr and accessorily rare earths, Ba, P, Ti, Zr. The ratio Nb/Ta is high. X-ray fluorescence was found very convenient to carry out these semi-quantitative analyses because the detection of the two characteristic elements Nb and Sr and also the value of the Nb/Ta ratio in carbonate rocks can be determined in a few minutes. Figures 4 and 5 show part of the X-ray fluorescence spectra taken on two pyrochlore carbonatites. The association Nb and Sr is very pronounced and Ta is only found in few amounts in these samples.

b) *Analysis of placer deposits.* Alluvial concentrates from the Lueshe and the Barreiro deposits were analyzed by X-ray fluorescence and show a high Nb/Ta ratio as well as an abnormal amount of strontium despite the easy lixiviation of this element by weathering. The strontium content of these concentrates ranges from 200 to more than 1,000 ppm, whereas it does not exceed 100 ppm in placer deposits derived from noncarbonatite sources. At Lueshe, we observed a close relationship between the strontium and the pyrochlore content in the alluvial concentrates around the carbonatite intrusions. Figure 6 shows an alluvial concentrate from Barreiro where an abnormal amount of strontium and a high Nb/Ta ratio were also recorded. X-ray fluorescence analyses of alluvial deposits give therefore valuable information concerning the presence of niobium-bearing carbonatites and are thus very useful in preliminary prospecting.

c) *Analysis of soils and superficial manganese-iron ores related to niobium-bearing carbonatites.* Residual and alluvial soils derived from niobium-bearing carbonatites exhibit a very pronounced geochemical secondary anomaly and can thus be used successfully in preliminary as well as in detailed prospecting. Soils derived from carbonatites show a marked enrichment in Nb. This feature was already observed by Fawley and James (28) in the Mbeya deposit where the niobium content of soils locally exceeds 1 percent of Nb_2O_5. At Lueshe and Barreiro, the niobium content of soils may exceed 2 percent

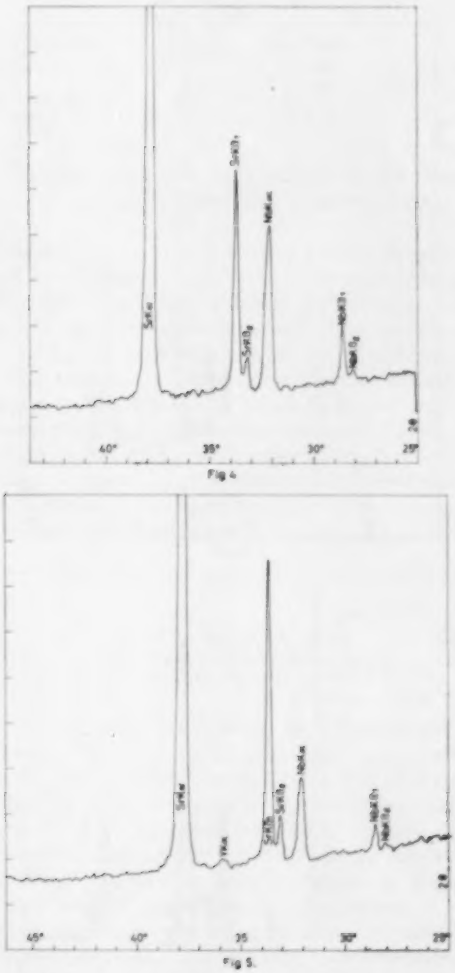


FIG. 4. Geochemical association of Nb and Sr in the niobium-bearing carbonatite of Lueshe.

FIG. 5. Geochemical association of Nb and Sr in the niobium-bearing carbonatite of Kaiserstuhl, Germany.

of Nb_2O_5. This enrichment is due mainly to a concentration of the resistant minerals pyrochlore, and perovskite, and also pyroxene in the case of Lueshe, in the residual soils by weathering. Strontium gives a characteristic geochemical anomaly despite its easy lixiviation by weathering. The strontium

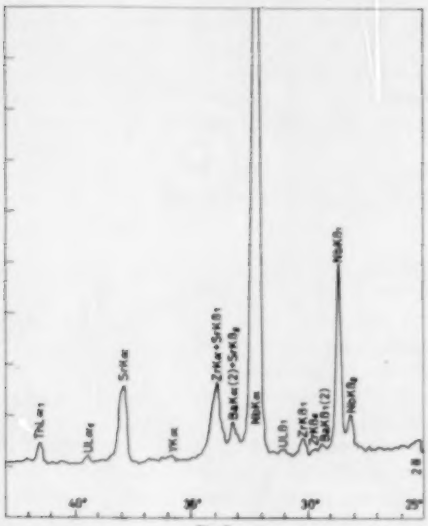


Fig 6

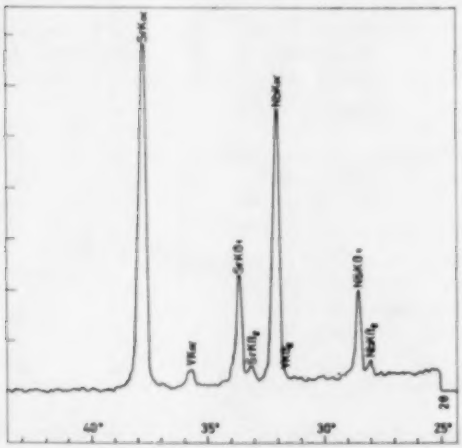


Fig 7

FIG. 6. Presence of abnormal amounts of Nb, Ba and Sr with Nb ≫ Ta in an alluvial deposit near the pyrometasomatic ore deposit of Barreiro, Brazil. The principal minerals are pyrochlore, magnetite, ilmenite, barite, limonite.

FIG. 7. Geochemical association of Nb and Sr in a manganiferous soil from the niobium-bearing carbonatite deposit of Lueshe.

TABLE I

Type of soils and locality		ppm Nb_2O_5	ppm SrO
Manganiferous soil Lueshe		7,400	7,100
Laterite	New ore deposit (Kivu)	11,590	3,250
Laterite		12,600	3,300
Laterite		11,000	3,300

content, however, is impoverished in soils relative to the parent carbonatites. Abnormal amounts of phosphorus are also observed locally in the soils of Lueshe.

The geochemical association of niobium and strontium with a high niobium-content and a high Nb/Ta ratio characterizes the soils from niobium-bearing carbonatites. This geochemical association is well illustrated by X-ray fluorescence spectra taken on a manganiferous soil from Lueshe (Fig. 7), on a soil of Barreiro (Fig. 8) and on a laterite from a new niobium-bearing carbonatite (Fig. 9). This geochemical association pointed out the existence of a new niobium-bearing carbonatite in the Kivu, Belgian Congo. Some results of a quantitative analysis by X-ray fluorescence made for niobium and strontium in soils from niobium-bearing carbonatites are given in Table I. Table II gives the average geochemical composition of the laterites from the new deposit for some elements. The weathering of iron-manganiferous carbonates, commonly present in the carbonatites deposits and also the iron or titan-

TABLE II

Content in ppm	Elements
10–200	Y, Zr, Th, U, Rb, Ta, Ba, Pb, Cu, Zn with Th > U
200–5,000	Ceric rare earth group, Sr
400–50,000	Fe, Mn, Ti, Nb with Nb ≫ Ta

ium minerals, hematite, magnetite, ilmenite, or rutile, give rise to superficial manganese-iron ores. The analysis of radioactive samples from such ores above the new carbonatite at Kivu, clearly shows that spectrographic analysis of superficial manganese-iron ores may allow the identification of concealed niobium carbonatites. Such analyses may yield valuable information concerning the geochemical associations found below the surface, and even the type of mineralization. The new carbonatite deposit at Kivu seems to have a more complex geochemical and mineralogical composition than the Lueshe deposit. The superficial oxides are manganiferous hematite, and manganese oxides associated with magnetite and ilmenite. In this oxide mass, association of niobium and strontium is characteristic but the concentrations are smaller than in the laterites. These oxides also contain metallic elements such as Co, Ni, Zn, Cu, Bi resulting probably from the weathering of sulfides or arsenosulfides. Their abundance varies widely from sample to sample. The content of niobium and strontium determined by X-ray fluorescence are as follows:

ppm Nb_2O_5	ppm SrO
425	2,360
535	2,380
1,335	1,480

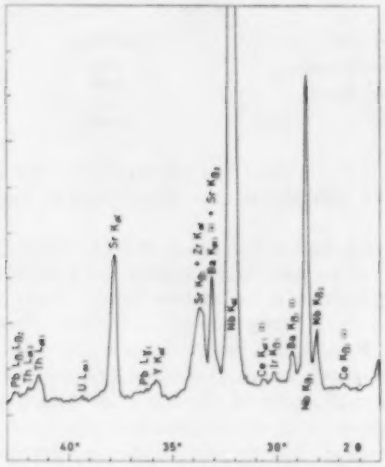


Fig 8

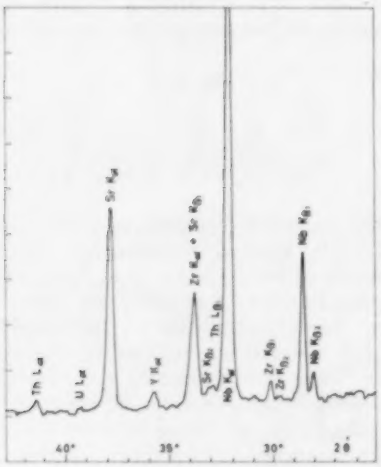


Fig 9

FIG. 8. Geochemical association of Nb, Sr and Ba in a radioactive soil from the pyrochlore deposit of Barreiro, Brazil.

FIG. 9. Geochemical association of Nb and Sr in a radioactive laterite from a new carbonatite deposit, Kivu, Belgian Congo.

The ratio Nb/Ta is very high as in the laterites. Table III gives the abundance of other chemical elements. It is not possible to determine whether these superficial manganese-iron ores were derived from veins, from localized

TABLE III

10–200 ppm	Y, Zr, U, Th, Ta with U > Th
5–15,000 ppm	Co, Zn, Bi, Cu, As, Ceric rare earths group
2,000–50,000 ppm	Ba, Ti
>50,000 ppm	Fe, Mn

masses, or dispersed grains in the carbonatites by the characteristic geochemical association Nb, Sr, rare earth, Ba, Ti and other elements. However, the superficial manganese-iron ores are important in the search for, and the prospecting of, carbonatites and vein deposits. Careful analysis and interpretation of fluorescence spectra may lead to interesting discoveries particularly in tropical countries like the Belgian Congo. Figure 10 shows part of the X-ray fluorescence spectra taken with a sample of superficial manganese-iron ore where abnormal amounts of Nb, Sr and Ba are observed (in this sample, only the second order of the K lines of Ba are visible).

Detailed Geochemical Prospecting

After the preliminary prospecting that determines the presence of a geochemical anomalous distribution of niobium, strontium and other interesting elements such as barium, or ceric rare earths, more careful and detailed sampling on 5-30 m grid is needed to define the extent and the intensity of the anomaly.

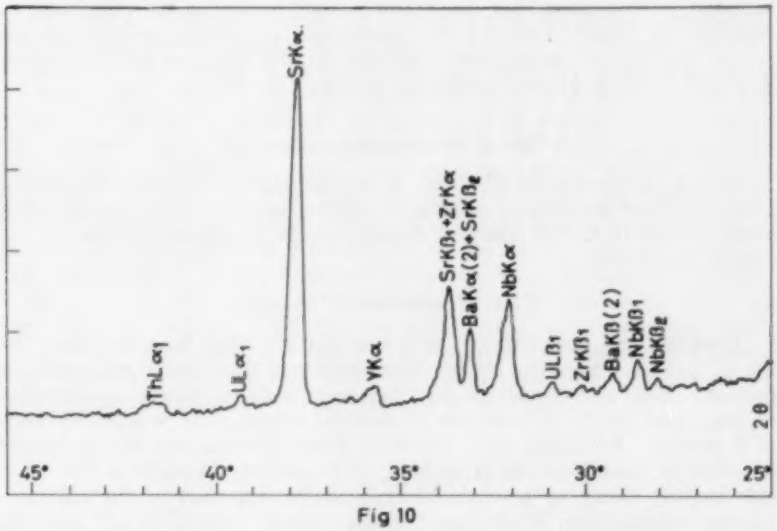


FIG. 10. Geochemical association of Nb, Sr and Ba in superficial radioactive iron-manganese ores from a new niobium-bearing carbonatite deposit, Kivu.

METHODS OF NIOBIUM ANALYSIS

Chemical Methods

Several chemical methods have been proposed for the determination of the niobium. *The absorptiometric methods* are mainly based on the absorbancy measurements of the yellow niobium thiocyanate complex and are commonly made after an extraction of the complex by a solvent (50, 51). This technique was used by Ward and Marranzino (52) for the detection of 25 to more than 2,000 ppm of niobium in rocks and soils. A thiocyanate-acetone method for niobium combined with a modified procedure for determining tantalum with pyrogallol was proposed by Marzys (53) to carry out both determinations on one sample solution. This method is now used in Central Africa for the determination of the niobium content of carbonatites and soils. The chemical analysis of niobium by the thiocyanate complex is difficult because several critical factors such as concentration, pH, temperature, and the stability of the complex interfere with the measurements and great care must be taken with these analyses (54). According to Prigogine (personal communication) a standard deviation of 10 percent is frequent in these analyses. Another absorptiometric method for the determination of the niobium is based on the yellow color produced by the addition of H_2O_2 to a sulfuric solution of the metal (55).

Hunt, North, and Wells (56) have developed a *paper chromatographic method* for the determination of small amounts of niobium in mineral samples. Its limit of detection is 4 ppm of niobium, its accuracy 50 percent and sixty samples can be analyzed per day. This method is used in Belgian Congo by Minière des Grands Lacs for the geochemical prospecting of niobium deposits. Similar chromatographic methods for the detection of niobium are described in the literature by different authors (57, 58).

Optical Spectrographic Methods

Optical spectrography (59, 60) is another classical method for the detection of small amounts of niobium in mineral samples but its sensitivity is variable from 10 to 100 ppm and depends on the apparatus and also on the matrix composition.

X-ray Spectrometric Methods

Campbell and Carl (61, 62) and also Mitchell (63) have described the use of X-ray spectrometry for the determination of the niobium and tantalum content. Most of the analyses described were made on mineral concentrates or were used for the examination of chemical preparations with an accuracy of 5 percent. Cavanagh (65) has used X-ray spectrometry for the determination of small amounts of niobium and tantalum. Stevenson (66) has also applied X-ray fluorescence analysis to the appraisal of the niobium-bearing carbonatite of North Bay, Canada.

In order to develop rapid as well as sufficiently accurate methods for the determination of the niobium in samples collected during geochemical pros-

pecting and for the appraisal of niobium-bearing carbonatites, the author re-examined the different methods of X-ray spectrometric quantitative analysis. The apparatus used is a Norelco Philips spectrometer equipped with a tungsten X-ray tube and a scintillation counter. Most of the measurements were made using a lithium fluoride analyzing crystal. The samples examined included carbonatites, soils and superficial iron-manganese oxides with 400 to more than 12,000 ppm of niobium oxide. To avoid errors due to grain size effects, the samples were grounded to pass a 200 mesh nylon screen. In the dilution and internal standard methods, where a defined amount of the comparison element is added to the sample, this mixture was homogenized in a multisample mixer.

The Internal Standard Method.—Hitherto this method has been the most used X-ray spectrographic method in quantitative analysis. The determination of the niobium content is made by comparison of the intensity of the NbKα line with the intensity of the reference line of the internal standard. The MoKα line has been used by the author as internal standard (see also references 61, 62, 66).

The basic equation is:

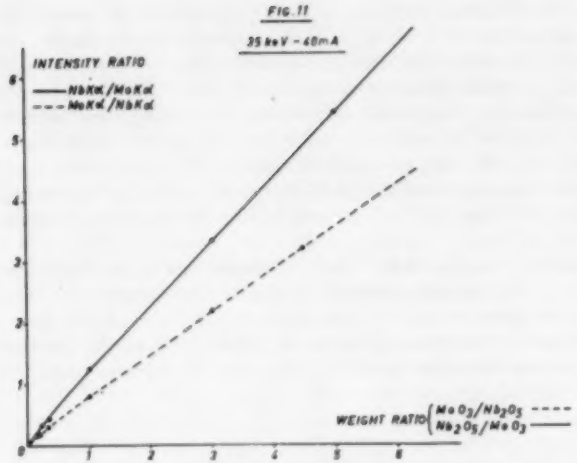
$$\frac{\text{NbK}\alpha}{\text{MoK}\alpha} = \text{K}\frac{\text{Nb}_2\text{O}_5}{\text{MoO}_3} \qquad \text{(equation 1)}$$

where K is a variable or a constant factor depending upon the resolving time of the whole scaler system.

A reference curve is obtained from a known mixture of Nb_2O_5 and MoO_3 in a matrix, by plotting the intensity ratio NbKα/MoKα versus weight ratio. The obtained curve is valid for all matrixes because the absorption of the characteristic fluorescent radiations of MoKα and NbKα is about the same for both lines which have adjacent wave lengths (MoKα = 0.709Å and NbNbKα = 0.747Å). However, the matrix cannot contain elements whose lines are between the two emission lines of NbKα and MoKα or between the K absorption discontinuities of the same elements (Mo = 0.619Å and Nb = 0.651Å). Figures 11 and 12 show the experimental points obtained from standard mixtures for 35 Kev and 45 Kev and for a scaler unit with a resolving time of 21 μsec. In this case, one obtains two curves passing through the origin. The K factor of equation 1 corresponds to the angular coefficient which varies with the value of the intensity ratio NbKα/MoKα. When the resolving time becomes negligible, the experimental points are very nearly on a straight line (Fig. 13) and the K factor is then practically constant. The standard deviation σ (see also reference 69) for each experimental intensity ratio can be obtained by the well known relation:

$$\sigma = \sqrt{\frac{\Sigma e^2}{n-1}} \qquad \text{(equation 2)}$$

where Σe^2 is the sum of the squares of deviation from the mean value of the whole set of measurements and n is the number of measurements. The standard deviation for the different values of the NbKα/MoKα ratio cor-



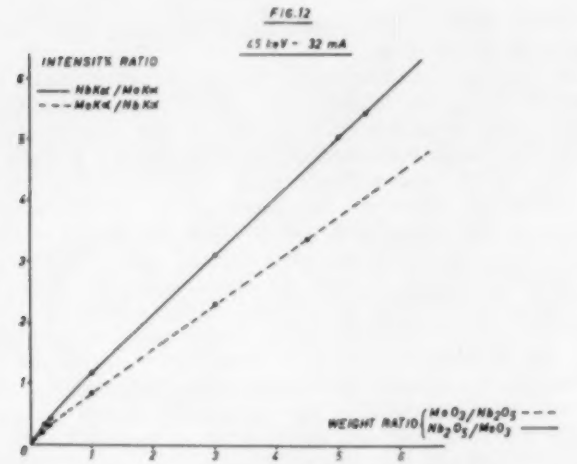


FIG. 11. *Internal standard method.* Curve obtained by means of standard samples for a voltage of 35 Kev and for a scaler unit with a resolving time of 21 μsec. Detector: scintillation counter-analyzing crystal: LiF (2d = 4,028).

FIG. 12. *Internal standard method.* Curve obtained by means of standard samples for a voltage of 45 Kev and for a scaler unit with a resolving time of 21 μsec. Detector: scintillation counter-analyzing crystal: LiF (2d = 4,028).

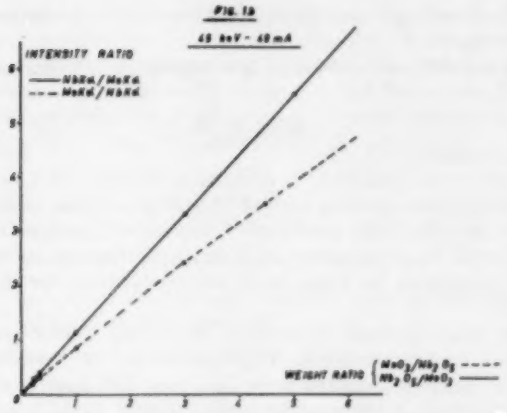


FIG. 13. *Internal standard method.* Curve obtained by means of standard samples for a voltage of 45 Kev and for a scaler unit with a resolving time of 1 μsec. Detector: scintillation counter-analyzing crystal: LiF (2d = 4,028).

rected for background, does not exceed 1 percent. For constant voltage, the reproducibility is excellent.

If the voltage varies, the intensity ratio NbKα/MoKα also varies. Figure 14 gives the value of the intensity ratio versus the voltage for a weight ratio equal to 1. This variation of the intensity ratio is due to the difference between the excitation voltage of NbKα and MoKα (MoKα = 17.50 Kev, NbKα = 16.50 Kev). The intensity ratio NbKα/MoKα will reach a con-

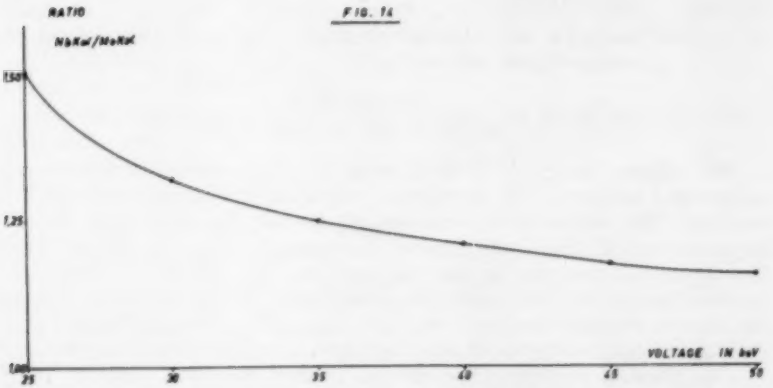


FIG. 14. *Internal standard method.* Variation of the intensity ratio NbKα/MoKα for a weight ratio equal to 1, with the voltage applied to the X-ray tube. Detector: scintillation counter-analyzing crystal: LiF (2d = 4,028).

stant value for a voltage four times higher than the excitation voltage, i.e. about 70 Kev (68).

The experimental points obtained are located on a hyperbola whose general equation is:

$$(x - x_0)(y - y_0) = A \qquad \text{(equation 3)}$$

where A is a constant.

For a weight ratio equal to 1, x_0 is equal to 15 Kev and y_0 is equal to 1.

The variation of the intensity ratio NbKα/MoKα versus voltage is of great practical importance in X-ray quantitative fluorescence analysis by the internal standard method. It is necessary in X-ray spectroscopy to work with the same voltage conditions as those used for establishing the standard curve (Figs. 11, 12).

During the determinations of niobium in mineral samples we have found some interfering lines, for example, YKβ and ULβ_1, but the contents of these elements in the samples analyzed were less than 100 ppm so these interferences were neglected in the measurements. Other possible interfering elements are the rare earths, Ce, La, Dy whose 2^d order Kα lines appear only when the voltage is more than 35 Kev. If the content of rare earths is greater, it is possible to avoid these interferences by reducing the voltage. Between the K absorption discontinuities of Mo and Nb we find the 2^d order ThLγ_2 and CeKβ_1, spectral lines. These elements do not interfere in our measurements. It is always convenient to examine by a rapid qualitative X-ray fluorescence analysis the possible interfering elements that may be present in the samples.

The niobium content is determined by the following equation:

$$\% \ Nb_2O_5 = \frac{\% \ MoO_3\alpha}{K} \qquad \text{(equation 4)}$$

where α = NbKα/MoKα.

K = The factor K is determined graphically by the line joining the origin to the point α.

$$\% \ MoO_3 = \frac{\text{weight } MoO_3}{\text{sample weight without } MoO_3} \text{ in } \%.$$

The samples analyzed by the internal standard method have been used as standard samples in the development of the other quantitative methods of analysis. The values found were verified by the dilution method and are in agreement with the results obtained by means of chemical methods. More than thirty samples can be analyzed per day for niobium by the internal standard method but the sample preparation takes a long time and therefore the internal standard method is not very efficient for the geochemical prospecting and also for the rapid appraisal of niobium-bearing carbonatites.

The Dilution Method.—The dilution method has been used by W. J. Campbell and H. F. Carl (62) for the determination of niobium and tantalum

[8] More complicated equations have been published in the literature by different authors (62, 69) but agree well with our formula.

in concentrates, and is based on the assumption that over a limited range there is a linear relationship between the intensity of the spectral line and the concentration of the corresponding element. The dilution technique requires measurement of the intensity of the spectral line of any element in the samples both before and after an addition of a known amount of this element.

The equation (62) is the following:

$$\frac{Ix}{I(x' + y)} = \frac{X}{XD + Y} \qquad \text{(equation 5)}$$

where Ix = line intensity of the element to be analyzed in counts/sec.

$I(x' + y)$ = intensity of the same spectral line after an addition of a known amount of this element.

Y = concentration of the dilution element.

X' = XD where D is a correction factor which takes into account the change of density due to the dilution of the sample.

The solution of equation 5 gives:

$$X = \frac{Ix \cdot Y}{I(x' + y) - Ix \cdot D}$$

For low dilutions (1 to 1.5%) D can be considered as about 1. In the case where the measured intensities Ix and $I(x' + y)$ are large, one must correct for counting losses due to the finite resolving time of the scaler unit.

The dilution method is only valid for concentrations of less than 3 to 4 percent and the best results are obtained when the ratio $Ix/I(x' + y)$ is about 0.5 to 0.7. However, this method is advantageous because the influence of possible interfering elements is negligible. Indeed, if they do exist, these interferences will affect both measurements in the same manner and consequently will cancel out in the calculation. Table IV gives the results obtained by the internal standard method and the dilution method on different mineral samples containing niobium.

The differences found in the first 3 samples are due to the very lowest value of the ratio $Ix/I(x' + y)$.

Thirty five to forty analyses can be performed per day by the dilution method.

TABLE IV

Samples	Internal standard method ppm of Nb_2O_5	Dilution method ppm of Nb_2O_5	Differences (in percent)
Manganese-iron oxides	435	470	+7.5
Manganese-iron oxides	535	580	+7.8
Manganese-iron oxides	1,335	1,420	+6.-
Laterites	11,590	11,500	−0.8
Laterites	12,600	12,600	—
Laterites	11,000	10,870	−1.2
Manganiferous soil	7,400	7,600	+2.7

The Direct Methods.—The direct counting methods have been used by Claisse and Cavanagh (64, 65) especially in trace elements analysis. In order to do a larger number of analyses per day, we have examined the possibilities offered by the direct methods in X-ray fluorescence analysis of niobium.

In the analysis by the direct methods the absorption of the characteristic fluorescence X-ray emitted (here NbKα) depends both on the chemical composition and the density of the matrix. Therefore, it is convenient to separate the mineral samples in three categories according to the chemical composition and the density of the matrix: 1) Iron-manganese oxides, 2) Carbonatites, 3) Lateritic soils.

Two direct methods of analysis have been tried with some variants, namely the direct counting method and the direct graphic method. As pointed out above, the reproducibility of the measurements is very high and therefore it is sufficient to do only a limited number of measurements. Thus the counting time is reduced and the efficiency increased. Moreover, no weighing is necessary.

The direct counting method like the direct graphic method is based on the assumption that a nearly linear relationship exists between the intensity of the spectral line and the concentration of the element to be analyzed in samples having a matrix similar in density and chemical composition.

The basic equations are very simple:

$$Ix = X$$

$$Iy = Y$$

where Ix = Intensity of the spectral line of the standard sample.

X = Known concentration of the corresponding element.

Iy = Intensity of the spectral line in the sample to be analyzed.

Y = Unknown concentration of the corresponding element.

The determination of the amount of any element in the direct counting method can be done in two ways: by direct comparison of the intensity of the spectral line with that of a standard sample or with a reference curve. The limit of detection depends primarily on the wave length, on the detector, on the kind of analyzing crystal, on the density of the matrix, on the voltage applied to the X-ray tube and to some extent on the perfection of the analyzing crystal, and of the goniometric system. For a scintillation counter and a lithium fluoride analyzing crystal, the limit of detection of the NbKα line was 15 ppm of Nb_2O_5 in the case of a relatively high density matrix like iron-manganese oxides. Figure 15 shows the linear relationship between the intensity of the NbKα line and known concentrations of Nb_2O_5. This curve subsequently served as a reference for the determination of the niobium content in the samples of iron-manganese oxides. Thus the determination of the trace elements can be done rapidly by comparison with a standard curve for a given matrix. Increased or decreased absorption of the characteristic fluorescence

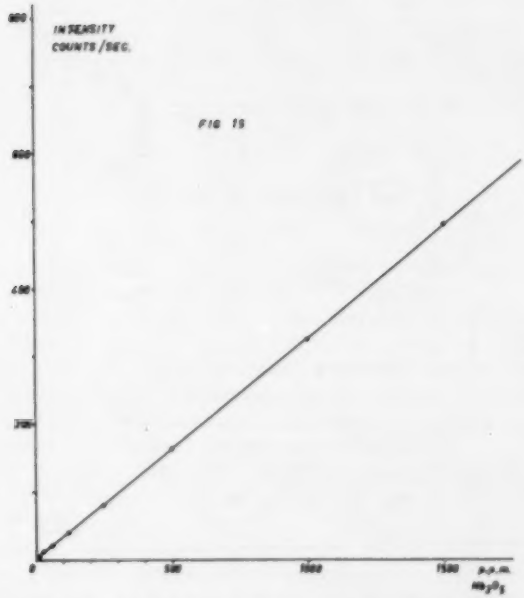


FIG. 15. *Direct counting method.* Linear relationship between the Nb_2O_5 content and the intensity of the NbKα line in counts per sec for standard samples. This curve was used for determining the amount of Nb in iron-manganese ores. Resolving time: 1 μsec. Detector: Scintillation counter-analyzing crystal: LiF (2d = 4,028).

X-ray radiation causes the straight line (Fig. 15) to be displaced correspondingly in the direction of positive or negative abscissa.

If the background measurements remain nearly constant for a given matrix (for instance carbonatite), it is possible to fix a mean value for the background and to eliminate back-ground measurement. Experimental work shows that the ratio of spectral line intensity to back-ground must be higher than 8. In this manner, we can increase notably the number of analyses performed per day (130 per day). The back-ground can also be reduced by the use of a single channel pulse height analyzer.

The direct counting method was successfully applied to the determination of niobium in soils, carbonatites and in the superficial iron-manganese oxides. The differences recorded in the percentages of niobium by comparison to the internal standard method are low (4 to 5 percent as a maximum). The measurements were made with a lithium fluoride analyzing crystal and by means of a pulse height analyzer. With the other analyzing crystals, the pulse height analyzer is not necessary.

Table V gives some results of niobium analysis in carbonatite samples made by the direct counting method. One of the samples in which the results

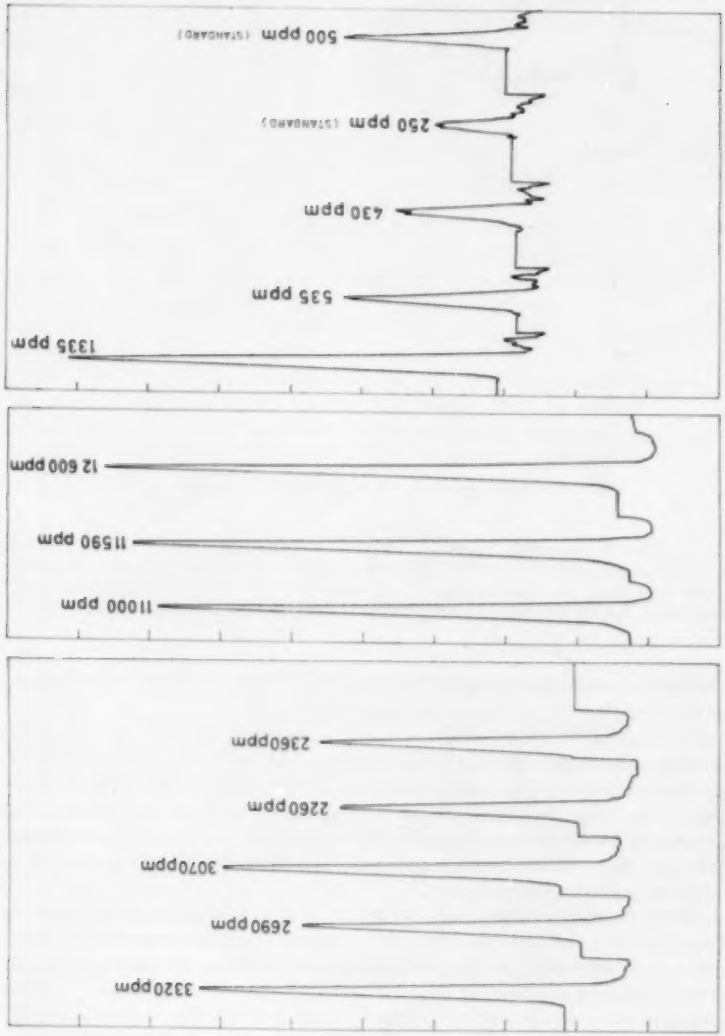


Fig 18
ppm of Nb_2O_5

Fig 17
ppm of Nb_2O_5

Fig 16
ppm of Nb_2O_5

TABLE V

Samples	Internal standard method ppm of Nb_2O_5	Direct counting method ppm of Nb_2O_5	Differences (in percent)
Standard	3,320		
1	2,690	2,600	−3.4
2	3,070	3,030	−1.3
3	2,260	2,187	−3.3
4	2,360	2,360	—
5	5,580	5,690	+1.8

were in good agreement with the results obtained by chemical analysis was chosen as the standard sample.

The direct counting method is very convenient for the rapid appraisal of the niobium content in carbonatites because of its accuracy and speed.

By the direct counting method, one can process 100 samples per day with back-ground measurements or 130 samples per day without background measurements. The intensity measurements are compared to that of one or more standard intensities (25 standard samples are taken per day).

In the *direct graphic method*, the spectral lines are recorded graphically on a paper and their lengths can be considered as approximately proportional to the concentration of the elements if the matrices have nearly the same density and chemical composition.

The inertia of the recording system is a supplementary error factor in the graphic measurements. Experimental works show that it is not possible to take it into account. The error, however, is only a few percent.

In using the *direct graphic method* most of the measurements were made with a pulse height analyzer. For each matrix and for a given spectral line the experimental conditions are chosen so as to obtain the maximum intensity for a given residual back-ground. The most important factors are the choice of the base-line and the channel width voltages. Less important are the voltage and the amperage of the X-ray tube. The intensity measurements are compared to a standard sample having a similar matrix to the samples to be analyzed. This standard sample is periodically used to correct for errors due to the possible small variations of the voltage and amperage applied to the X-ray tube. The sensitivity for trace elements analysis is not as high as in the direct counting method, for example, it is 30 ppm of Nb_2O_5 in an

FIG. 16. *Direct graphic method.* Determination of the niobium content of carbonatite samples by the direct graphic method using a pulse height analyzer. The sample containing 3,320 ppm of Nb_2O_5 was taken as a reference sample (base line: 12.50 V—channel width: 6.45 V—X-ray tube: W, 50 Kev, 45 mA—analyzing crystal: LiF—NbKα line).

FIG. 17. *Direct graphic method.* Determination of the niobium content in soils from niobium-bearing carbonatites by the direct graphic method using a pulse height analyzer (base line: 12.60 V—channel width: 6.45 V—X-ray tube: W, 50 Kev, 45 mA—analyzing crystal: LiF—NbKα line).

FIG. 18. *Direct graphic method.* Determination of the niobium content in superficial iron-manganese ores by the direct graphic method using a pulse height analyzer (base line: 12.60 V—channel width: 5.45 V—X ray tube: W, 45 Kev, 40 mA—analyzing crystal: LiF—NbKα line).

TABLE VI

Internal standard method ppm of Nb_2O_5	σ%	σ 90% = 1.64 × σ
3,320		
2,260	5.31	8.71
2,360	6.01	9.85
5,590	6.10	10.00
3,070	2.44	4.00

iron-manganese oxide matrix, because of the loss of intensity due to the use of the pulse height analyzer. The reproducibility of the measurements on a set of samples was quite good. Table VI gives the standard deviation of these measurements with reference to results obtained by the internal standard method for a set of carbonatites samples analyzed by comparison with a standard (3,320 ppm).

Figures 16, 17, 18 show the graphic recording of the NbKα line in the case of carbonatites, laterites and superficial iron-manganese ores. These measurements were taken with a pulse height analyzer. The error on the measurements appears to be larger than in the other X-ray fluorescence methods. The direct graphic method, however, has the advantage of reducing the calculations and thereby increasing the number of analyses made per day, per man (200 analyses). Because of its high efficiency, the direct graphic method is suitable for rapid appraisal of the niobium content in geochemical prospecting and in some extent for quantitative evaluation of niobium-bearing carbonatites.

Efficiency and Accuracy of the Different Methods of Niobium Analysis

It is useful to compare the efficiency, the accuracy and the limit of detection for the different methods of niobium analysis. The data are assembled in Table VII.

TABLE VII

X-RAY SPECTROGRAPHY

	Internal standard method	Dilution method	Direct counting method	Direct graphic method
Number of samples per day and per man	30–35	35–40	100 or 130*	200
Limit of detection Nb (in ppm)		5–20	5–20	20–45
Accuracy (in percent)	2 to 6	3 to 7	8	12

OTHER METHODS

	Optical spectroscopy	Absorptiometry	Paper chromatographic method	Extraction method of Ward and Marranzino
Number of samples per day and per man	80–100	20	60	30–40
Limit of detection Nb (in ppm)	10 to 100	?	4	25
Accuracy (in percent)	Variable	2 to 10	50	15 to 20

* 100 with back-ground measurements—130 without back-ground measurements.

The accuracy for all methods is generally and directly related to the complexity of the chemical composition of the materials and in particular to the presence of interfering elements. The accuracy diminished for concentrations less than 1,000 ppm.

Table VII indicates clearly the advantages of X-ray fluorescence analysis for the determination of the niobium content especially in geochemical prospecting and for the appraisal of niobium-bearing carbonatites. On the other hand, the X-ray quantitative methods described here are applicable to a wide range of niobium content and moreover, difficult chemical separations are avoided. The limit of detection may also be improved by the use of a curved analyzing crystal (70).

CONCLUSIONS

X-ray methods were successfully applied to the study of the mineralogy and the geochemistry as well as to the preliminary or the detailed prospecting of niobium-bearing carbonatites. They can also be used for the appraisal of niobium ore deposits.

The mineralogy and the geochemistry of the carbonatite deposits are easily studied by the use of the X-ray diffraction-fluorescence method. The geochemical association of Nb and of Sr with other elements, such as Ba, rare earths, Ti, Zr, etc., was used for the prospecting of carbonatites and its application led to the discovery of a new niobium-bearing carbonatite in the Kivu, Belgian Congo. Two direct methods of X-ray fluorescence analysis were developed for the determination of the niobium content in rock and soil samples. They are rapid and sufficiently accurate to permit their use for the appraisal of niobium-bearing carbonatite.

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THE TERNARY SYSTEM Ag_2S-Bi_2S_3-PbS [1]

H. J. VAN HOOK

ABSTRACT

Phase equilibria in the systems Bi-S, Ag_2S-PbS, Ag_2S-Bi_2S_3, PbS-Bi_2S_3, $AgBiS_2$-PbS, and Ag_2S-Bi_2S_3-PbS have been studied by thermal analysis and quenching methods. The high solid solubility of bismuth and silver in the synthetic galena-type structures is correlated with the common occurrence of these elements in natural galena.

INTRODUCTION

STUDIES of argentiferous galena deposits (13) have shown that galena commonly contains minute inclusions of silver minerals that occur in galena as irregular inclusions or as lamellae. The lamellar intergrowths are commonly considered to represent unmixing during cooling as a result of decreasing solid solubility at low temperatures (27).

Individual silver minerals have not been found in some silver-producing ore deposits (21) and here the silver is probably held in solid solution in ore minerals such as galena and tetrahedrite.

Because of the minute size of the inclusions in most argentiferous galena, a positive identification of silver mineral, or minerals, is often not possible, and argentite has generally been assumed to be responsible for the silver content in these ores. The discovery that argentite is only slightly soluble in galena (22) left the question unanswered as to why argentite should be preferentially incorporated as minute disseminated bodies in a mineral in which it is so sparingly soluble.

Ramdohr (27) studied the mineralogy of argentiferous galena extensively and found that the most common inclusions are sulfosalts of silver, not argentite, as had been previously assumed. Furthermore, the sulfosalts commonly occur as lamellar inclusions parallel to certain crystallographic planes in galena, suggestive of unmixing, whereas argentite inclusions are generally irregular or rounded in shape. Intergrowths of galena and matildite ($AgBiS_2$) (Fig. 1) have provided a particularly good example of unmixing in galena solid solutions as specimens have been found in which the sulfosalt phase occurs in amounts sufficient to permit a positive identification. Ramdohr's studies (26) of these intergrowths indicated that solid solution of matildite in galena may be extensive, especially at high temperatures, and that the textures observed are due to a decrease in solubility related to a structural change in matildite at low temperatures.

The majority of the known sulfosalts can be grouped compositionally as

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FIG. 1. A natural intergrowth of β matildite (white lamellae) and galena (dark phase) solid solution. Ramdohr (1938), 70 ×.

sulfides of lead, copper, silver, and one or more of the group V_b elements: arsenic, antimony, or bismuth (25). Although structurally complex, they appear to be related to the simple sulfide structures such as galena or sphalerite by a distortion to varying degrees of these close-packed "basic" structures. Ross (30) and Hellner (15) have discussed the relationship between simple "basic" and variously complex "derivative" structures of sulfides and sulfosalts. The usefulness of this approach is best shown by those minerals that have inversions to high temperature polymorphs isostructural with one of the "basic" sulfide structures (4, 30). This is true of the silver sulfosalts matildite ($AgBiS_2$), and aramayoite ($Ag(BiSb)S_2$), and miargyrite ($AgSbS_2$), all of which have been reported to transform at about 200° C from complex low-temperature forms to high-temperature galena-type structures (11).

Trace element studies as reported by Fleischer (6) have shown that antimony, bismuth, and silver are the most common constituents in galena and, in some cases, are present in amounts up to several percent. Oftedahl (23) observed that the amount of these elements present in galena is greater in the "high temperature" deposits. He found (24) that solid solutions containing silver and bismuth in equal molecular proportions are indistinguishable from normal galena in polished section but that samples containing more

bismuth than silver are distinctly anisotropic and exhibit octahedral parting in contrast to the usual (001) cleavage. These properties have been attributed to charge imbalance resulting from the atomic substitution of Bi^{+3} for Pb^{+2} (24), or to oriented exsolution intergrowths in the host mineral (34).

Taken together, the mineralogical and chemical studies suggest that argentite is only slightly soluble in galena, whereas bismuthinite and certain silver sulfosalts have much higher solubilities and that the lamellar intergrowths arise from decreasing solid solubility at low temperatures.

Despite the detailed mineralogical studies on galena intergrowths, no systematic experimental investigation of solubilities and phase relations has been made which might unify and coordinate these observations. Accordingly, phase equilibrium studies in the system Ag_2S-Bi_2S_3-PbS were undertaken to establish the solubility of silver sulfide and bismuth sulfide in galena and galena-type solid solutions.

Crystalline Phases in the Ternary System

Minerals reported in the system Ag_2S-Bi_2S_3-PbS are shown in Table 1 and Figure 2. The table has been compiled principally from Palache et al. (25) except where otherwise noted and includes only those minerals whose compositions fall within the ternary system, Ag_2S-Bi_2S_3-PbS. Other synthetic phases such as α $AgBiS_2$, $Ag_2S \cdot 3Bi_2S_3$, $(Ag_2S)_1$, are also given.

EXPERIMENTAL PROCEDURE

Mixtures used in this study were prepared from "zone purified" lead and bismuth (99.99% Pb and Bi), reagent grade silver powder, and Baker U.S.P. flowers of sulfur.

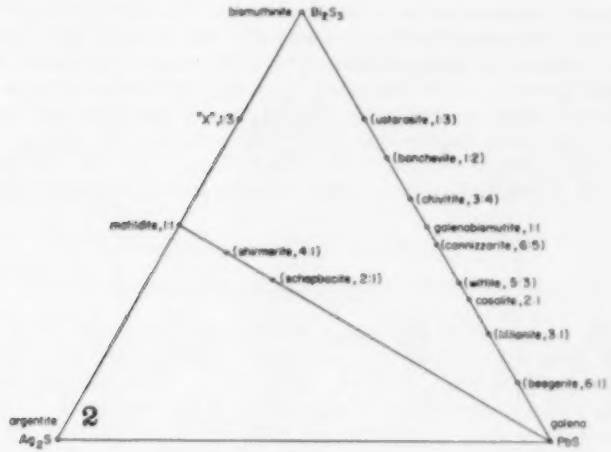
Ten-gram samples of the end-member compositions were first prepared by sealing sulfur and metal mixtures under vacuum in clear silica glass tubes and slowly heating to above the melting temperature. The sulfur in the silica tube was melted at about 120° C before sealing to reduce the volume of the sulfur plus metal reactants, thereby permitting a seal with a small space above the charge. Free space above the sulfide samples was kept as small as possible to avoid the necessity of adding excess sulfur to compensate for vapor loss. After complete melting, the products were examined by x-ray diffraction and in polished section for homogeneity before being combined in weighed amounts to give the desired binary and ternary compositions.

Liquidus, solidus, and some subsolidus temperatures in the system were determined by differential thermal analysis using apparatus described by Keith and Tuttle (18). The sulfide compositions previously synthesized were sealed in silica glass vials having a reentrant in the base for a differential couple. A heating rate of 4°/minute was maintained by a motor-driven variac. Cryolite (transition 563° C, 18) and sodium chlorite (melting point, 801° C) were used as calibration standards for the differential thermal heating experiments. The temperature of the phase transitions was taken as the beginning of the differential-thermal peak on heating. All of the transitions

TABLE 1

CRYSTALLINE PHASES REPORTED IN THE SYSTEM Ag_2S-Bi_2S_3-PbS

Mineral	Composition	Crystal structure	Remarks
—	$(Ag_2S)_I$	Unknown	Stable above inversion temperature (592° C). For compositional range and corresponding inversion temperatures, see Kracek (20). Displacive inversion to $(Ag_2S)_{II}$(argentite).
Argentite	$(Ag_2S)_{II}$	Cubic, Im3m $a_0 = 4.88$ Å	Found only as pseudomorph: stable in temperature range 592–176° C. Displacive inversion to $(Ag_2S)_I$.
Acanthite	$(Ag_2S)_{III}$	Orthorhombic (?)	Stable naturally occurring form of Ag_2S. Pseudomorphs of argentite have the acanthite structure.
Galena	PbS	Cubic Fm3m $a_0 = 5.93$ Å	
α Matildite	$Ag_2S \cdot Bi_2S_3$	Cubic Fm3m $a_0 = 5.64$ Å	Not found in nature. Stable form above 195° C; isostructural with PbS. For composition range, see Figure 12. Sluggish inversion to matildite.
β Matildite	$Ag_2S \cdot Bi_2S_3$	Orthorhombic or hexagonal	Studied by Graham (11) and Geller and Wernick (9) by single crystal x-ray methods.
—	$Ag_2S \cdot 3Bi_2S_3$	Monoclinic (C-centered)	Not reported in nature. Discovered in this study.
Schirmerite	$4AgBiS_2 \cdot PbS$	Unknown	Ramdohr (27) has reported a non-cubic pattern for the only known specimen.
Schapbachite	$2AgBiS_2 \cdot PbS$	Unknown	Original material found to be a mixture of galena and β matildite (27).
Beegerite	$6PbS \cdot Bi_2S_3$	Cubic (?)	Symmetry on the basis of morphology; no definite evidence of homogeneity. Ramdohr (27) reports that much, if not all beegerite is argentian.
Lillianite	$3PbS \cdot Bi_2S_3$	Orthorhombic (?)	Berry (2) reported lillianite to be a mixture of galenobismutite and galena; original material also a mixture of sulfides. Kobellite may be an antimonian variety.
Cosalite	$2PbS \cdot Bi_2S_3$	Orthorhombic Pbnm	A fairly common mineral in mesothermal and contact metamorphic deposits.
Wittite	$5PbS \cdot 3Bi_2S_3$	orthorhombic or monoclinic (?)	Needs further study; single known occurrence in amphibolite.
Cannizzarite	$6PbS \cdot 5Bi_2S_3$ (?)	Monoclinic	Graham (12) gave monoclinic indices for synthetic and natural material; possibly identical with galenobismutite.
Galeonobismutite	$PbS \cdot Bi_2S_3$	Orthorhombic Pnam	In volcanic fumeroles with bismuthinite and in other high temperature deposits.
Chivitite	$3PbS \cdot 4Bi_2S_3$	Orthorhombic (?)	Needs confirmation—some specimens are a mixture of bismuthinite and other sulfides.
Bonchevite	$PbS \cdot 2Bi_2S_3$	Orthorhombic (?)	Kostov (19); in contact metamorphic deposit.
Ustarasite	$PbS \cdot 3Bi_2S_3$	Unknown	Mentioned by Kostov (19).
Bismuthinite	Bi_2S_3	Orthorhombic Pbnm	Typically found in hydrothermal veins "formed at relatively high temperatures" and in pegmatites.



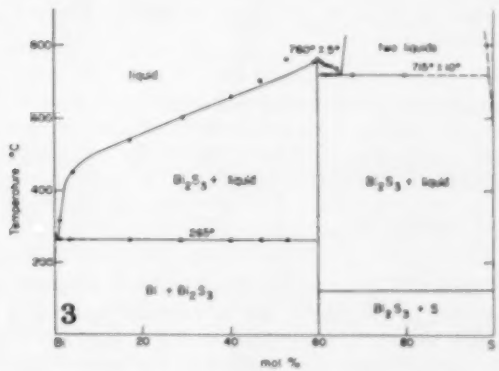


FIG. 2. Crystalline phases reported in the system Ag_2S-Bi_2S_3-PbS.
FIG. 3. Phase diagram Bi-S at the pressure of the system. Open circles are DTA temperatures, dots are from Schenck and Pardun (1933).

measured on cooling were found to be within 5° C of this value with the single exception of the Bi_2S_3 composition which supercooled about 50° C. The value recorded for the phase change was determined by the intersection of a line drawn through the trace of the background with a line through the first straight portion of the trace for the heat effect. All compositions were run at least twice and the results were found to be reproducible to within ± 2° C on heating.

Quenching runs were made in conjunction with the DTA investigation to identify the phases present and to establish solid solution limits. For this

work samples were sealed in silica glass tubes and, after holding at a given temperature, were quenched by dropping the tube directly into water. The accuracy of the temperature measurement in these runs is probably ± 2° C.

Quench products were examined by x-ray diffraction using a Norelco Wide Range Diffractometer with filtered copper radiation and a separate silicon mount as a calibration standard. The accuracy of d-spacing measurements is believed to be ± 0.002 Å for reflections above 50° 2θ. Samples were also studied in polished sections using a standard metallographic microscope.

RESULTS OF THE INVESTIGATION

The System Ag-S

Kracek (20) studied the binary system Ag-S in detail using methods similar to those described above. He found a single compound, Ag_2S which melts congruently at 838 C ± 2° and extensive liquid immiscibility at melting temperatures for compositions on either side of the compound. The partial vapor pressure of Ag_2S in equilibrium with Ag° at the melting temperature is reported by Richardson and Jeffes (29) to be 10^{-6} at m., indicating that the decomposition by loss of sulfur to the vapor in sealed containers is negligible under these conditions.

TABLE 2

PHASE TRANSITION TEMPERATURES IN Ag_2S ON HEATING

	Transition $(Ag_2S)_{III}$-$(Ag_2S)_{II}$	Transition $(Ag_2S)_{II}$-$(Ag_2S)_{I}$	Melting point
Kracek	176.7° C ± 0.6°	593° C ± 3°	838° C ± 2°
This study	175° C ± 5°	590° C ± 5°	835° C ± 5°

Experimental Results.—The phase transition temperatures in stoichiometric Ag_2S measured in this study are in essential agreement with those given by Kracek as is shown by a comparison of the results in Table 2. Several separately prepared samples of the stoichiometric Ag_2S composition showed a very small excess of silver which formed dendrites of hair silver when the charge was cooled to room temperature. Kracek reported similar results for silver-rich compositions. The excess silver present in these preparations, however, could be the result of errors in weighing or loss of sulfur vapor to the space above the charge and does not prove non-stoichiometric Ag_2S.

The System PbS

A study of this system by Bloem and Kröger (3) has shown that PbS is the only compound. Lead sulfide melts at 1077° C ± 5° at a total pressure ($P_{Pb} + P_{S_2}$) of 0.3 atm. whereas the maximum melting composition with 0.03 mol % excess Pb melts at 1,127° C ± 5° at 0.1 atm.

The melting point of PbS as measured in the present study (1,115° C ± 5°), is only in fair agreement with the reported value; this is probably due

to the extreme variation in melting temperature for metal-rich compositions near PbS. The temperature recorded is presumably that of a composition intermediate between PbS (1,077° C) and $Pb_{1.0002}S_{0.9997}$ (1127° C).

The System Bi-S

Phase equilibria in the system Bi-S are complicated by the relatively high vapor pressures generated at melting temperatures, particularly for the compound (Bi_2S_3) and for sulfur-rich compositions, and were not studied in previous work. The available data on Bi-Bi_2S_3 compositions (1) are shown in Figure 3.

Experimental Results.—The results of the differential thermal study of nine compositions are shown in Figure 3. The maximum melting (760° C ± 5°) composition corresponds to the compound Bi_2S_3, which melts at an estimated vapor pressure of 1–5 atm. Since the vapor above the charge is probably sulfur-rich, the composition of the condensed phases (solid and liquid Bi_2S_3) may be somewhat deficient in sulfur. Considering the known vapor pressure of sulfur, the mol fraction of sulfur in Bi_2S_3, and the molal volume of the container, i.e., the degree of filling of the vial, the change in composition of Bi_2S_3 at 760° C cannot exceed a loss of 0.5 mol % S and is probably much smaller than this value.

As sulfur is added to Bi_2S_3, the liquidus temperature is lowered to 715° C ± 10° and remains constant at this value for compositions having more than 65 mol % S. At high temperatures a vapor phase was observed above the condensed phases for all of these compositions. There appeared to be two possible phase relationships involving non-condensed binary equilibria which could give rise to the heat effect at 715° C: 1) Intersection of the three-phase surface, compound plus liquid plus vapor, or 2) intersection of the quadruple invariant point involving the compound, two liquids, and vapor.

Discussion of the Results.—The effect of the total pressure must be taken into account in any discussion of the phase relations because of the high vapor pressures generated in the melting range. The PT, TX, and PX projections of the assumed PTX (pressure-temperature-composition) space model of the system are shown in Figure 4. The system contains a congruently melting compound and a region of liquid immiscibility. The curves L_1CV and CL_2V in the PT projection represent univarient three-phase surfaces giving temperatures and pressures at which the compound Bi_2S_3 is stable together with a liquid and a vapor phase. The values given on the L_1CV surface were calculated from data by Schenck and Pardun (31). The curve C = L is the congruent melting curve of the compound. The univarient curves in the one-component systems, bismuth (17), and sulfur (16), are shown by dashed lines. The curves in the projection representing the surfaces of three coexisting binary condensed phases (SCL_2, $BiCl_1$ and CL_1L_2) are relatively insensitive to pressure changes and appear as straight lines essentially parallel to the pressure axis. This is in contrast with the pressure-sensitive CL_2V, L_1CV, and L_1L_2V surfaces where vapor is present. Isobaric sections ($(TX)_p$) through the PTX model are shown for several pressures in Figure

4. The TX section at P_1 is a schematic representation of the phase diagram at one atmosphere.

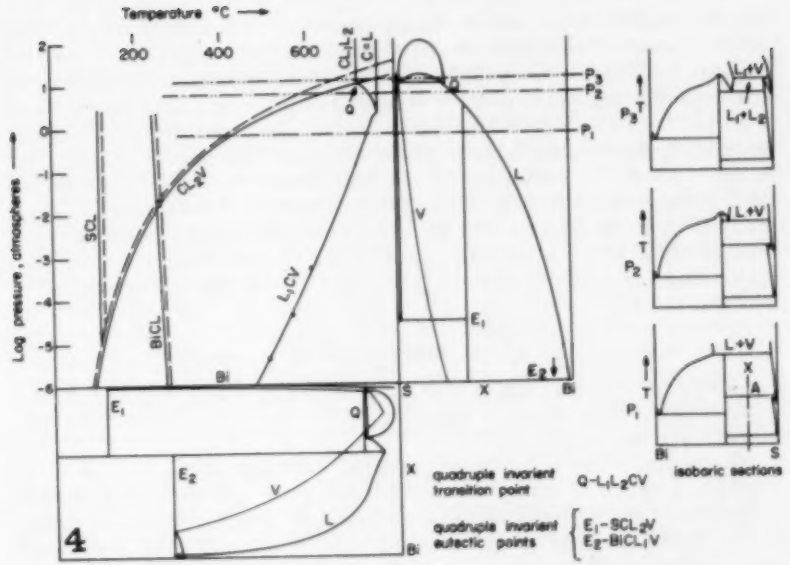
A discussion of the phase equilibria in terms of a PTX model does not apply directly to the experimental conditions in the present study as pressure is not an independently controlled parameter under conditions of constant volume. Pressure is generated internally and varies with temperature as well as with the molal volume of the phases present, and the relative molal volume of each phase is in turn dependent on the bulk composition (37). It is therefore necessary to consider the modifying effect of constant volume on the phase equilibria in PTX representation.

In isobaric ($(TX)_p$) sections of the binary system a composition such as X for pressure P_1 in Figure 4 is condensed at temperatures below the intersection with the three-phase surface (A), the containing vessel being collapsed by externally applied pressure. At the intersection temperature for any given pressure the assemblage changes isothermally from Bi_2S_3 plus liquid to Bi_2S_3 plus vapor (at A), and the container expands at constant pressure to accommodate the vapor phase.

In constant volume ($(TX)_v$) sections for the same binary mixture, however, vapor is present in the space above the sample over a wide range of temperatures and pressures, except for the limiting case where the thermal expansion of the condensed phase or phases reduces the available free space to zero. Assuming the liquid and vapor in these mixtures to be nearly pure sulfur, the CSV (compound + sulfur (S) + vapor) and CLV surfaces will probably parallel closely the L = V curve for pure sulfur in pressure and temperature (Fig. 4). Consequently compositions such as X (Fig. 4) at constant volume will consist of three phases whose total pressures are slightly less than those given by the L = V curve for pure sulfur at various temperatures, resulting in what is essentially a polybaric section through the binary system following this curve. The extent of departure of the CLV surface from the sulfur boiling point curve depends upon the amount of bismuth in the sulfur-rich vapor; the amount is unknown and may actually cause significant deviation, particularly at high temperatures.

It is evident from the preceding that the sulfur vapor pressure in equilibrium with bismuth sulfide-sulfur mixtures is not negligible at high temperatures and that the free space above the charge must be kept as small as possible to avoid significant losses of sulfur from the condensed phases. For this reason relatively large amounts of samples (1 gm) were used for the DTA study and an attempt was made to maximize the degree of filling of the vials.

For any given temperature and binary composition it is assumed that the three-phase surface, CLV, is limited to pressures below the boiling point curve for pure sulfur and to temperatures below the maximum melting composition (Bi_2S_3) at 760° C. Within this range of temperature and pressure, there appeared to be two possible phase relationships that might give rise to the heat effect observed at 715° C: (1) A continuous CLV solubility surface with a pressure maximum, or (2) the formation of two immiscible liquids involving a quadruple point Q (Fig. 4). The latter possibility is considered



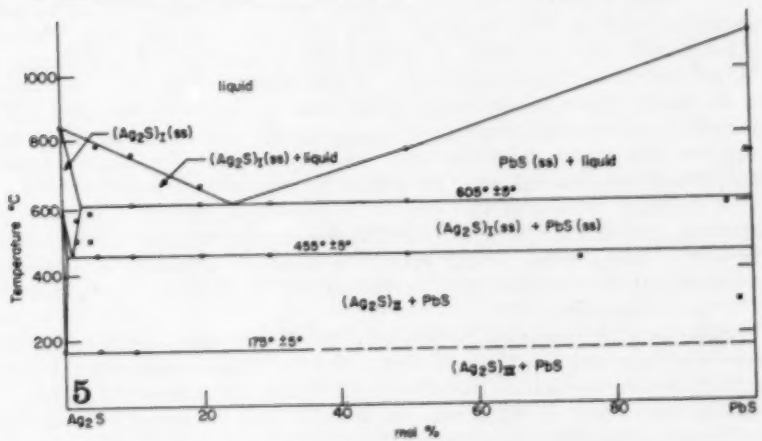


FIG. 4. Projections of the PTX model for the binary system Bi-S.

FIG. 5. Phase relations in the system Ag_2-PbS. In all phase diagrams in this paper, open circles (○) represent DTA temperatures, dots (·) one phase regions, triangles (△) liquid plus crystals, squares (□) two crystalline phases, and crosses (+ single phase boundary lines.

to be more likely for two reasons: 1) In the case of the continuous CLV surface, the intersection temperature at constant volume must change with increasing sulfur content and increasing pressure. The heat effect recorded, however, remained essentially invariant for all Bi_2S_3-S compositions as shown in Figure 3. The constancy of this transition temperature, on the other hand, is expected if liquid immiscibility is present, giving rise to a quadruple point *Q* (Fig. 4). 2) It is improbable that one liquid plus vapor are present above the reaction temperature because of the resulting high density required for the vapor phase. A calculation of the vapor density in equilibrium with one liquid phase with 65 mol % sulfur, (Fig. 3) gave a density value approximately 30 times as large as that given for pure sulfur vapor in the presence of liquid sulfur at the same temperature (715° C) indicating again that two liquids are more probable than one above 715° C for these sulfur-rich compositions.

The System Ag_2S-PbS

Liquidus relations in this system were studied by Friedrich (7). It is a simple binary system having a eutectic at 23 wt. % PbS. The eutectic temperature was reported as 630° C.

Nissen and Hoyt (22) investigated the solubility of Ag_2S in PbS by preparing a series of synthetic mixtures that were quenched from various temperatures; the fusion products were examined along with several argentiferous galena samples in polished sections. They identified very small rounded spots of argentite as a second phase under high magnification in both the natural and synthetic material. The maximum solubility was reported as less than 0.6 percent at 800° C in the synthetic samples, and approximately 0.1 percent in the galena specimens as determined by an assay for silver on the latter. More recent studies of argentite inclusions by Ramdohr (27) confirm the experimental findings of Nissen and Hoyt, although Ramdohr has suggested that smaller solubility limits are more probable, i.e., about 0.1 percent at high temperatures and 0.01 percent at low temperatures.

It should be noted here that very small amounts of bismuth (and possibly antimony, arsenic, etc.) as "impurities," in the starting materials used to make the binary compositions, would greatly increase the solubility of silver as indicated both by mineralogical observations and by the experimental results to be given presently.

Experimental Results.—The results of this investigation, presented in the form of a phase diagram (Fig. 5), are essentially in agreement with the findings of previous workers. The effect of PbS solid solution on the high-temperature heat effect in Ag_2S was found to be quite pronounced, lowering the inversion from 590° C for pure Ag_2S to 455° C for the Ag_2S solid solution. The differential thermal heat effect was also noticeably broadened by solid solution. The inversion in Ag_2S at 175° C, however, was not measurably changed by the presence of excess PbS.

The solubility limits of PbS in Ag_2S were studied by the quenching method using polished sections to identify the phases. The maximum solubility at

the eutectic temperature (605° C) was found to be 3 mol % PbS. At 455° C, the inversion temperature of the maximum solid solution, the solubility is approximately 2 mol percent and below the inversion the solubility is considerably less than 2 percent as shown by exsolution blebs of PbS which appeared in Ag_2S quenched from above the inversion temperature.

The solubility of Ag_2S in PbS was also studied by the quenching method. A sample containing 0.5 mol % Ag_2S quenched from 700° C showed a trace of argentite in polished section, and comparison of X-ray data on this sample with PbS held at the same temperature showed a measurable difference in the lattice constants. Using a slow scanning speed on the X-ray diffractometer, the peak displacement indicated a change in the lattice constant of 0.0020 Å which is believed to represent a solubility of 0.4 mol % Ag_2S from $AgBiS_2$-PbS solubility data.

Discussion.—Solid solution of PbS in Ag_2S lowers the higher temperature inversion in Ag_2S by 135° C but has no measurable effect on the inversion at 175° C. This difference is probably a result of the relatively high solubility of PbS in $(Ag_2S)_I$ and the much lower solubility in $(Ag_2S)_{II}$ (argentite).

The solubility limits of Ag_2S in PbS are of particular interest in the present study and an X-ray method has been developed to determine the solubility avoiding the limitations of microscopic detection of a second Ag_2S phase. Since solid solution in PbS is very limited in the binary system, a direct determination of solubility using unit cell variation by preparng PbS-AgS mixtures was not feasible. A value of 0.4 mol % Ag_2S at 700° C was calculated by extrapolating the change in the lattice parameter of ternary Ag_2S-PbS-$AgBiS_2$ solid solutions and is probably close to the assumed maximum solubility at the binary eutectic temperature (615° C). These results are consistent with the limiting value of less than 0.6% Ag_2S proposed by Nissen and Hoyt (22).

The System Ag_2S-Bi_2S_3

Gaudin and McGlashan (8) studied a series of synthetic fusion products in the binary system Ag_2S-Bi_2S_3. The samples were heated to the melting range, cooled very slowly to room temperature, and then examined in polished sections. On the basis of the textural relationships found, the authors proposed a tentative phase diagram with a congruently melting "phase D" ($3Ag_2S \cdot Bi_2S_3$) corresponding to the rare mineral tapalpite, and the compound matildite ($Ag_2S \cdot Bi_2S_3$) which was believed to melt incongruently. Leutwein and Herrmann (21) prepared several synthetic Ag_2S-$AgBiS_2$ compositions but could find no indication of the "phase D" reported by Gaudin and McGlashan; they questioned the validity of its existence in the binary system, pointing out that the only known sample of tapalpite contains a considerable amount of tellurium.

The mineral matildite was first described in detail by Ramdohr (26). He found that the compound $Ag_2S \cdot Bi_2S_3$ has a polymorphic transition at 210° C, the low temperature form (β matildite) having orthorhombic symmetry and the high temperature form (α matildite) being cubic. The inversion tem-

perature ($\beta \rightarrow \alpha$) was determined by heating the mineral (β $AgBiS_2$) on a high temperature X-ray unit. The inversion in matildite was re-examined by Graham (11) using both natural and synthetic specimens. Samples prepared by fusion and by hydrothermal techniques yielded α matildite which was converted to the low-temperature form by heating at 180° C for 9 days. Graham concluded that the change in symmetry is due to an inversion ($\alpha \rightarrow \beta$) and that the body-centered orthorhombic form is related to the high temperature face-centered cubic form by a slight distortion of the cubic lattice parameters. More recent work by Geller and Wernick (9) has indicated that the β form is hexagonal rather than orthorhombic.

Experimental Methods.—The phase boundaries of α $AgBiS_2$ and Ag_2S solid solutions were located by examination of polished sections. Variation of the cell dimensions of α matildite was used to confirm the results of the microscopic study and to extend the determination of Ag_2S solubility from the inversion in $AgBiS_2$ at 195° C to the melting point. The presence of excess Bi_2S_3 did not measurably affect the cell size of α $AgBiS_2$ and this phase boundry was located only approximately by microscopic examination.

Experiments dealing with the matildite inversion were carried out with samples in sealed tubes and with powdered material contained between two glass slides, i.e., open to the atmosphere. A comparison of X-ray patterns indicated that oxidation did not occur in the samples exposed to the atmosphere and that both of these annealing methods could be used to elucidate the phase relations at low temperatures. Grinding the samples after annealing was avoided since the reflections corresponding to Ag_2S are obliterated by this process; they reappear, however, upon further annealing.

Experimental Results.—The results of this study which are summarized in the phase diagram, Figure 6, are quite different from those of Gaudin and McGlashan (8). There was no indication of a "phase D" at melting temperatures and X-ray studies of runs held several months at 170° C have failed to show any evidence of this compound at low temperatures. A compound not reported by Gaudin and McGlashan having a composition $Ag_2S \cdot 3Bi_2S_3$ was found in the system; it appears to have no mineralogical equivalent. No evidence could be found for polymorphism or solid solution in this phase.

Matildite melts congruently at 801° C ± 5° and shows a large range of binary solid solution. Solid solution of Ag_2S in $AgBiS_2$ increases the cell constant from 5.640 Å to 5.706 Å (± 0.002 Å) at the eutectic temperature (615° C) where 10 mol % Ag_2S is dissolved in the crystalline phase, and decreases with decreasing temperature as shown in Figure 6 to 1.7 mol % Ag_2S at 200° C. Solid solution of 16 mol % Bi_2S_3 to stoichiometric $AgBiS_2$ does not change the size of the unit cell of the phase to a measurable degree (± 0.001 Å) although the diffraction peaks of quenched samples are more diffuse than the reflections for α $AgBiS_2$.

The solubility of Bi_2S_3 in $(Ag_2S)_1$ is 4 mol % at the eutectic (615° C). As in the system Ag_2S-PbS, solid solution lowers the high temperature transition in Ag_2S (from 590° to 522° C) but causes no measurable change in the argentite-acanthite inversion.

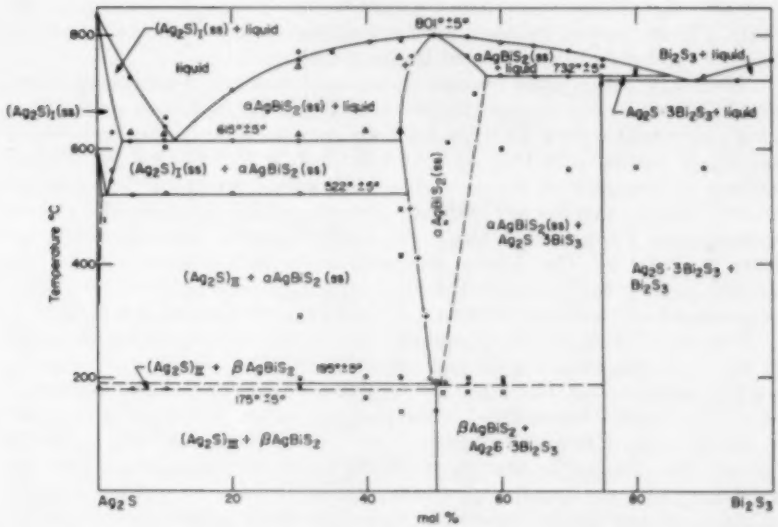


Fig. 6. The system Ag_2S-Bi_2S_3. Note extensive solubility in $\alpha AgBiS_2$.

The matildite inversion: The phase transition in matildite was studied using quenching techniques and thermal analysis. X-ray investigation of quenched samples indicated that the transition occurs reversibly at 195° C ± 5° in less than one week for $AgBiS_2$ and for binary mixtures of Ag_2S and α or β matildite. The conversion takes place more slowly (several weeks) for mixtures of α or β matildite and the $Ag_2S{\cdot}3Bi_2S_3$ phase and here the inversion has been determined within the range 170°–200° C. Differential thermal analysis revealed a very small but reproducible heat effect in α matildite with excess Bi_2S_3 at 190° C for samples containing 52, 55, and 60 mol % Bi_2S_3 but not for $AgBiS_2$. Twin lamellae were also observed in these bismuth-rich matildite compositions at room temperature, but disappeared upon heating above 190° C.

Extra diffraction peaks were found in β matildite which do not correspond to d-spacings indexed by Graham (11) and may be identical to those which he attributed to uncombined Ag_2S and removed from the diffraction patterns of his synthetic product. These additional peaks were found both in the assemblages $\beta AgBiS_2 + (Ag_2S)_{III}$ (30, 40, and 45 mol % Bi_2S_3) and in mixtures identified as $\beta AgBiS_2 + Ag_2S{\cdot}3Bi_2S_3$ (55 and 60 mol % Bi_2S_3) as well as in $\beta AgBiS_2$ (Fig. 6) and disappeared entirely when these compositions were held above the inversion temperature. The diffraction peaks in question are marked with an asterisk in Table 3 which gives a comparison of the d-spacings observed with results quoted by Graham. More recent X-ray studies by Geller and Wernick (9) indicate that $\beta AgBiS_2$ is hexagonal

and not orthorhombic, their data compare favorably with the findings in this study. There was no evidence for the intermediate rhombohedral phase between α- and β-$AgBiS_2$ predicted by these authors.

The $Ag_2S \cdot 3Bi_2S_3$ phase: Single crystal oscillation and Weissenberg photographs were taken of cleavage fragments of $Ag_2S \cdot 3Bi_2S_3$ heated several days in a sealed tube with a KCl-NaCl salt mixture as a flux. The unit cell is monoclinic having $a_0 = 13.3$ Å, $b_0 = 4.05$ Å, $c_0 = 16.5$ Å, $\beta = 94°$; Weissenberg photographs of the zero, first, and second reciprocal lattice layers about b indicate that the cell is C face-centered, belonging to one of the three space groups, $C2$, Cm, or $C2/m$. The indexed powder diffraction data are given in Table 4. The density, measured on a one-half gram sample, was 6.8 ± 0.5, using the pycnometer method with methylene iodide ($\rho = 3.325$), as compared with a calculated density of 6.72 for a cell containing $4(AgBi_2S_5)$.

Fragments of $Ag_2S \cdot 3Bi_2S_3$ generally occur as thin plates that are elongated in the b direction with a good cleavage at about 15° to b. The direction of the longest repeat distance, taken as c, is approximately normal to the cleavage or parting surface responsible for the platy character. Cleavage is only fair in this direction (001), the surfaces of the tabular fragments being generally curved. In polished section $Ag_2S \cdot 3Bi_2S_3$ is strongly anisotropic and has a tendency to form equant grains as compared with the very much stronger anisotropism and acicular habit of Bi_2S_3 and the weak anisotropism of Bi-rich α $AgBiS_2$ solid solutions.

TABLE 3

COMPARISON OF POWDER DIFFRACTION DATA ON SYNTHETIC $AgBiS_2$

Graham (1951) "Ag-S lines removed"			Present study	
d-spacing (kX)	Intensity (CuKα)	Calculated (hkl)	d-spacing Å	Intensity (CuKα)
			6.86*	2
			3.46*	2
3.29	8	011	3.30	8
3.16	1	101	3.17	3
2.82	10	110,002	2.83	10
			2.58*	1
			2.15*	0.5
2.03	6	020	2.03	6
1.967	5	200	1.969	6
			1.937*	0.5
			1.732*	2
1.708	3	121,013	1.714	3
1.670	0.5	211	1.672	1
1.648	0.5	022	1.650	2
			1.600*	0.5
1.586	0.5	202	1.583	0.5
			1.553*	0.5
1.411	1	004,220	1.414	1.5
1.316	1	031	1.319	1
1.282	1	130	1.281	1
1.247	1	310	1.248	1

* d-spacings not reported by Graham.

TABLE 4

SINGLE CRYSTAL DATA ON $Ag_2S \cdot 3Bi_2S_3$

Observed d-spacings (Å)	Intensity (CuKα)	Calculated d-spacings (Å)	Observed d-spacings (Å)	Intensity (CuKα)	Calculated d-spacings (Å)
5.45	3.5	5.49 (003)	2.585	1	2.617 (206)
					2.560 (313)
5.32	1.5	5.40 (202)			
			2.460	2	2.477 (404)
4.08	3	4.06 (203)			
		4.11 (004)	2.338	1	2.352 (007)
		4.05 (010)			
			2.259	3.5	2.239 (405)
3.86	0.5	3.87 (110)			2.266 (116)
3.59	9	3.59 (204)	2.206*	1	2.208 (600)
					2.212 (406)
3.52	0.5	3.54 (11$\bar{2}$)			
			2.115	1	
3.46	4	3.47 (112)			
			2.014	3	
3.38	8	3.36 (204)			
			1.989	0.5	
3.31	3	3.31 (400)			
		3.30 (401)	1.393	0.5	
3.27	2	3.29 (005)	1.804	1	
3.22	0.5	3.20 (11$\bar{3}$)	1.728	1.5	
3.18	0.5	3.17 (40$\bar{2}$)	1.421	0.5	
		3.19 (401)	1.301	0.5	
3.12	0.5	3.16 (113)	1.166	0.5	
2.98	1	2.98 (310)			
2.955	3	2.967 (31$\bar{1}$)			
		2.953 (403)			
2.858	10	2.851 (205)			
		2.863 (312)			
2.761	1.5	2.754 (312)			
		2.744 (006)			
2.727	.5	2.732 (403)			

* Spacings were not calculated for reflections below this value.

Discussion.—The structure of $\alpha AgBiS_2$ can be derived from that of galena by substitution of $Ag^{+1} + Bi^{+3}$ for $2Pb^{+2}$ where the silver and bismuth atoms are randomly distributed in the octahedral sites. Large amounts of either Bi_2S_3 or Ag_2S in excess of the 1 : 1 composition can be held in the structure at high temperatures, possibly as substitutional solid solution of the atomic constituents in the same octahedral positions, although the mechanism of solid solution is probably much more complex and may involve interstitial positions.

Assuming substitutional solid solution, the increase in cell dimensions of $\alpha AgBiS_2$ with added Ag_2S may be qualitatively accounted for by a comparison in size of the ionic radii (Ag = 1.12 Å and Bi = 1.1 Å, Goldschmidt, 1955) and covalent radii (Ag = 1.53 Å and Bi = 1.46 Å, Pauling and Huggins, 1934), assuming some intermediate ionic-covalent bonding in these structures. Using this reasoning, an excess of Bi_2S_3 should decrease the unit cell size: however, cubic $AgBiS_2$ with 16 mol % excess Bi_2S_3 has the same cell dimen-

sions as does the pure compound. The assumption of substitutional solid solution with excess Ag_2S or Bi_2S_3 introduces the additional problem of accounting for an excess or deficiency of metal atoms in the octahedral positions. Alternatively, solid solution may be interstitial in the tetrahedral sites between four sulfur atoms (and four metal atoms), although the radii of bismuth and silver as cited above indicate a rather close fit in these positions. The sulfur-metal distance in $\alpha AgBiS_2$ is 2.44 Å in the tetrahedral positions as compared with 2.82 Å for octahedral coordination.

Addition of either Ag_2S or Bi_2S_3 to the compound requires a charge balance by some mechanism within the solid to maintain the original cubic structure, possibly by the creation of positive or negative "holes." The fact that such extensive electronic adjustments can be made is a further indication of the complex, non-ionic nature of the bonding.

The inversion in matildite: The temperature of the inversion (195° C) in $\alpha AgBiS_2$ is not measurably changed by the presence of excess Ag_2S or of Bi_2S_3 although the rate of inversion shown by quenching results is altered significantly. X-ray powder diffraction patterns of binary mixtures held for different periods of time both above and below the inversion interval have indicated that the inversion in Ag_2S-rich compositions and in $AgBiS_2$ requires several days to go to completion whereas with excess Bi_2S_3, the inversion takes several weeks.

Profuse twinning was observed in polished sections of α-matildite prepared in the presence of excess Bi_2S_3 and disappeared on heating above 190° C. At approximately this same temperature a heat effect was detected by differential thermal analysis. Both of these changes were observed on material which the X-ray powder diffraction patterns have shown to be cubic or nearly cubic and therefore do not represent changes that can be related to the sluggish $\alpha \leftrightharpoons \beta$ inversion of matildite. These changes in Bi_2S_3 saturated matildite were not observed in stoichiometric $AgBiS_2$ or in Ag_2S saturated material. It is suggested that these changes are due to a metastable displacive transformation in Bi_2S_3 saturated αmatildite, which fortuitously takes place at a temperature near the stable matildite inversion.

The System PbS-Bi_2S_3

As the primary objective of this investigation was to study the solubility of silver in galena together with phase equilibrium relations among silver-bearing phases or minerals and galena, the system PbS-Bi_2S_3 was of secondary interest and only a few experiments were carried out with these compositions. The solubility of Bi_2S_3 in galena was studied in some detail, however, to locate the limits of solid solution along the PbS-Bi_2S_3 sideline.

Evidence for appreciable solubility of Bi_2S_3 in galena may be found in the mineralogical literature. Oftedal (24) described galena samples containing several per cent bismuth from ore deposits that are believed to have formed at high temperature. Leutwein and Herrmann (21) reported increasing bismuth content with depth in the Freiberg ore deposit without finding any discrete bismuth mineral to account for the increase. They concluded that

bismuth is held in solid solution in the galena ore and that with increasing depth the higher temperature portion of the deposit is being reached in the mining operation. They prepared synthetic PbS compositions containing 2.5 and 5 wt. % Bi_2S_3 and reported a decrease in the galena cell constant with solid solution.

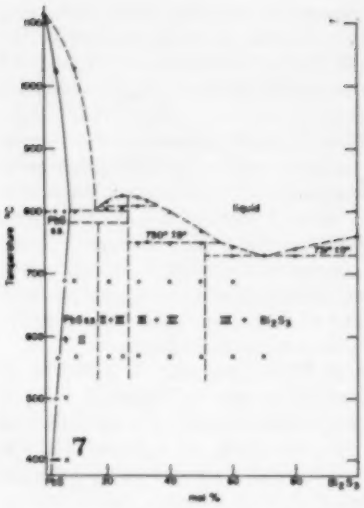
Experimental Methods.—The solubility of Bi_2S_3 in galena was determined by the quenching method using polished sections and x-ray diffraction techniques. The cell dimensions of galena were found to decrease approximately 0.004 Å for each 1 mol percent Bi_2S_3 held in solid solution for mixtures containing 0, 4, 7, and 10 mol % Bi_2S_3 quenched from 800° C. The composition of the galena solid solution at various temperatures was then deduced from a measure of the position of the diffraction peaks. For experiments at 500° and 400° C, a solid solution and a mixture of PbS and Bi_2S_3 were run together to assure that equilibrium solubility was being measured.

Experimental Results.—The solubility of Bi_2S_3 in galena is 9 mol % at 800° C and decreases at lower temperatures as shown in Figure 7. Equilibrium was not completely attained for the different starting materials held at 400° C and the solubility could only be given limits of 1–3 mol %. At 500° C the original solid solution and the mixture of PbS and Bi_2S_3 gave the same value for the galena lattice parameter.

Binary compositions higher in Bi_2S_3 in the system were studied by X-ray methods and by polished sections and are tentatively shown in Figure 7.

Discussion.—The mineralogical studies suggest a definite correlation between high formation temperatures and high bismuth content in galena. The experimental data support this hypothesis, as the results have shown that solid solution is appreciable at low temperatures and increases with rising temperature. The change in cell dimensions with solubility of Bi_2S_3 may be used as an indicator of minimum formation temperature only if the composition is strictly binary (PbS-Bi_2S_3) and if a second lead sulfosalt phase is present. Small amounts of silver have a pronounced effect on cell dimensions as will be shown presently, while the effect of other "impurities" such as copper, antimony, selenium, and tellurium (10) is unknown and may be significant. Solid solution of various elements may also stabilize galena beyond the solubility limits in this system. For example, a galena phase corresponding to the composition given for beegerite (14.3 mol % Bi_2S_3, Table 1) is not stable in binary compositions as the maximum solid solution at the eutectic is 9 mol % Bi_2S_3, but a ratio of PbS to Bi_2S_3 of 6:1 is quite possible in ternary or quaternary compositions.

The octahedral parting of bismuthian galena in polished section described by Oftedal (23) and Wahlstrom (34) was not observed in the synthetic compositions. The most likely explanation for the parting in galena is that it results from growth of exsolution lamellae along octahedral directions. Apparently the lamellae did not develop sufficiently in synthetic mixtures to give rise to the octahedral parting or to permit microscopic identification. The fact that the lamellae were not visible, however, does not imply that equilibrium solubility was not measured, as solubility was established independently by



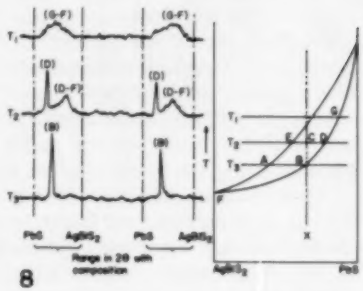


FIG. 7. The system PbS-Bi_2S_3.
FIG. 8. Schematic X-ray patterns for composition X in the system $AgBiS_2$-PbS quenched from different temperatures.

X-ray measurements on different starting materials held at the same temperature.

Additional experimental work is needed on the Bi_2S_3-rich portion of this system. The synthetic analogues of the known sulfosalt materials (Table 1) were not found in this study and apparently form by subsolidus reaction below the temperatures investigated. It is also possible that equilibrium was not attained in these compositions. In any event, the determination of the subsolidus stability relations would be useful in the interpretation of these phase assemblages in nature.

The System $AgBiS_2$-PbS

The mineralogical studies of matildite-galena ($AgBiS_2$-PbS) intergrowths by Ramdohr (26) have demonstrated that solid solution is extensive in this system. He described matildite-galena intergrowths in detail and proposed that unmixing of high temperature solid solutions is related to the matildite inversion. Although no systematic study of binary unmixing temperatures was made, Ramdohr assumed that the general form of the solvus could be deduced from the mineralogical information; he estimated that the solubility of $AgBiS_2$ in galena is approximately 14 mol % at a temperature below that of the inversion in matildite.

Chapman and Stevens (5) described a galena sample which contained: "numerous minute inclusions of a strongly anisotropic mineral which . . . are lath shaped and look as if they had been deposited from a solid solu-

tion in the host mineral." The composition of the sample was given as $Ag_2 \cdot Bi_2S_3 \cdot 11PbS$, corresponding to 15.4 mol % $AgBiS_2$. The powder diffraction photograph was shown, but no other X-ray data were given. Ramdohr (26) subsequently identified this second phase as matildite and may have used this specimen in his estimate of the solubility of $AgBiS_2$ in galena (14 mol %) at low temperature.

Leutwein and Herrmann (21) carried out some experimental work on the system in connection with their geological studies of the Freiberg ore deposit. They prepared a synthetic composition containing 2 mol % $AgBiS_2$ ($a_0 = 5.914$ *kX*) demonstrating that the lattice constant of galena ($a_0 = 5.922$ *kX*) decreases with solid solution. They concluded that solubility is extensive if not complete at high temperatures, which was later confirmed by Wernick (36).

Experimental Methods.—Liquidus-solidus equilibria were investigated by a quenching method that will be described in some detail since it appears to have general applicability in systems of this type. The method utilizes the lattice changes as a function of composition in conjunction with fractional crystallization induced by quenching.

In binary systems having complete solid solution, mixtures cooled from the region of solid plus liquid generally crystallize with some fractionation, the amount of fractionation depending on the rate of cooling. The liquid phase continuously changes composition with falling temperature during this process and approaches the composition of the lowest melting mixture. With rapid cooling, the residual liquid in a mixture such as "X" (Fig. 8) is intermediate between the composition of the residual liquid formed under equilibrium conditions (*A*, Fig. 8) and the final liquid resulting from complete fractionation (*F*, Fig. 8). Because of the pronounced change in the lattice constant with change in composition in this system, fractional crystallization in quenched charges is reflected in the X-ray diffraction patterns.

Applications to the present study: 1) Solidus temperatures were determined by holding solid solutions at successively higher temperatures until a change was detected in the position of the diffraction peaks of the solid phase on quenching. At higher temperatures the solidus could then be located from the composition of the primary crystals in quenched samples (viz. T_3, Fig. 8).

2) The "fractionation" quenching method was also used to decide whether the system $AgBiS_2$-PbS has a minimum on the liquidus. The existence of a binary minimum would be shown by the trend in composition of the liquid during fractional crystallization, i.e., towards the mixture having the lowest melting temperature.

3) For mixtures near $AgBiS_2$, the liquid phase crystallized essentially without fractionation giving relatively sharp diffraction peaks and it was possible to locate liquidus as well as solidus composition by measuring the position of the peaks corresponding to both of the quenched phases.

Experimental Results.—Results of the study of the binary system are shown in Figure 10. Miscibility at high temperatures is complete as was

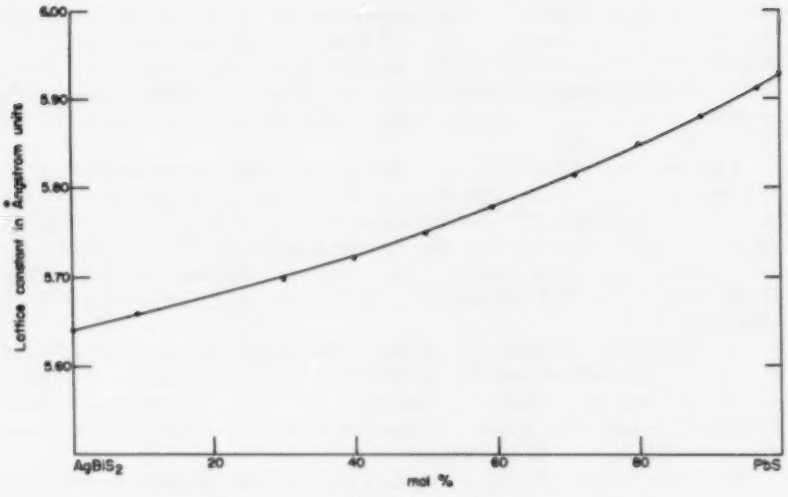


FIG. 9. Lattice constant of $AgBiS_2$-PbS solid solutions.

predicted by previous investigators. The variation in unit cell constant with composition for the binary solid solutions is shown in Figure 9. The system is represented as $AgBiS_2$-PbS to conform with the binary join the ternary system, although the assumed substitution, Ag^{+1}, $Bi^{+3} = 2Pb^{+2}$, indicates that the system should be considered as $AgBiS_2$-2PbS.[1] Liquidus and solidus curves were located by the quenching technique and X-ray analysis described in the preceding section. Differential thermal analyses were made as a check on the quenching results and were found to be in good agreement (Fig. 10). Diffraction patterns of mixtures near $AgBiS_2$ all indicated progressive crystallization with residual liquids approaching $AgBiS_2$ with falling temperature, indicating that there is no minimum in the system. For this particular investigation, it was necessary to cool the samples more slowly (in air rather than in water) because of the tendency of these liquids to quench without fractionation.

Runs were made at low temperatures for periods up to several months in an effort to determine more precisely the position of the solvus proposed by Ramdohr (26). In general, unmixing of the solid solutions is so sluggish that equilibrium could not be realized. Samples near $AgBiS_2$ in composition, however, did reveal some tendency to change to the stable low-temperature assemblage. A charge containing 3.9 mol % PbS held for three months at 170° C contained about 2 percent galena in polished section. A second sample with 10 mol % PbS was found by X-ray study to consist of a partially inverted high temperature solid solution along with smaller peaks corresponding

[1] Representation as $AgBiS_2$-PbS results in a positive deviation from Vegard's Law rather than negative as in Fig. 9.

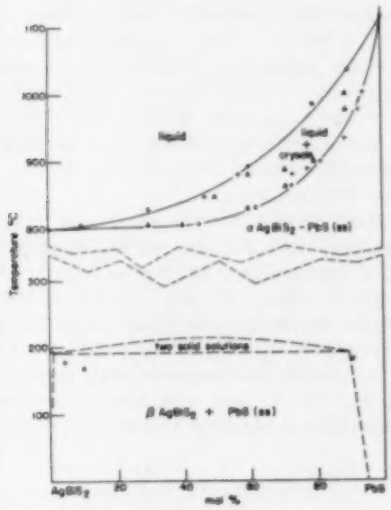


FIG. 10. The system $AgBiS_2$-PbS. Note break in the temperature axis.

to a second, galena-rich phase containing 10 mol % $AgBiS_2$. Compositions with a higher PbS content did not transform to the low-temperature assemblage.

Discussion.—Solid solution is complete at high temperatures in this system: solidus and liquidus temperatures rise continuously from the melting point of $AgBiS_2$ (801° C ± 5°) to that of PbS (1115° C ± 5°). The quenching technique described is considered to be preferable to thermal analyses as the results can be related to equilibrium conditions, avoiding possible errors due to superheating or supercooling of the sample. The principal error inherent in the method is that quenching may not be rapid enough to prevent reaction of the liquid with the primary crystals and that the measured solidus composition would then be higher in $AgBiS_2$ than the equilibrium value. Preliminary studies on the influence of quenching rate, however, showed that any partial reaction is reflected in a definite skewness of the diffraction peaks for the primary solid phase. A sharp peak for the solid separated by an interval from the diffuse peak representing the quench crystals was taken as evidence that no reaction had occurred between phases on quenching.

Unmixing of the solid solutions below solidus temperatures is extremely sluggish and was generally unsuccessful except for compositions near $AgBiS_2$. Ramdohr's studies (*26*) of galena-βmatildite intergrowths, however, have provided information on natural material from which the solubility in galena below unmixing temperatures can be calculated. He prepared X-ray powder photographs of a specimen from the Mayflower Mine, Ontario and found that the calculated cell constant for the galena phase in the intergrowth was

$a_0 = 5.89$ kX. He apparently assumed that this value should correspond to that of pure PbS ($a_0 = 5.93$ kX) and that the X-ray camera was inaccurate. He then "corrected" the calculated elements for the matildite phase by the factor 5.93/5.89. Graham (11) subsequently synthesized matildite and found that the cell dimensions ". . . agree poorly with those given by Ramdohr (26), after halving and interchanging his a and b periods." The discrepancy in the data is considerably reduced if Ramdohr's uncorrected values are compared with Graham's findings, viz.:

It is evident from these results that the correction which Ramdohr applied should not have been made and that the material examined was a galena solid solution whose lattice constant is near the measured value of 5.89 and not 5.93 kX, the "corrected" value. Taking 5.89 kX as the cell dimension and using the data compiled in the present study (Fig. 9), the galena phase in the intergrowth corresponds to a synthetic solid solution containing 8 mol % $AgBiS_2$. This value may be compared with the experimental measurement of 10 mol % at 170° C, and with the observation of Chapman and Stevens (5) that a specimen containing 15.4 mol % $AgBiS_2$ is an intergrowth of two phases.

The System Ag_2S-Bi_2S_3-PbS

Experimental Methods.—DTA methods were used to determine the melting relations in this system. Solid solution in matildite-galena structures was determined by examination in polished section of mixtures that were held at ternary solidus temperatures before quenching. In the composition triangle Ag_2S-$AgBiS_2$-PbS solidus temperatures are between 592° and 615° C depending on the composition whereas in the area Bi_2S_3-$AgBiS_2$-PbS, the ternary invarient temperatures are unknown and were estimated from a knowledge of the melting relations in the binary system PbS-Bi_2S_3.

The variation in lattice constant with composition, as determined by X-ray measurements of peak position on the quenched ternary solid solutions is shown in Figure 11.

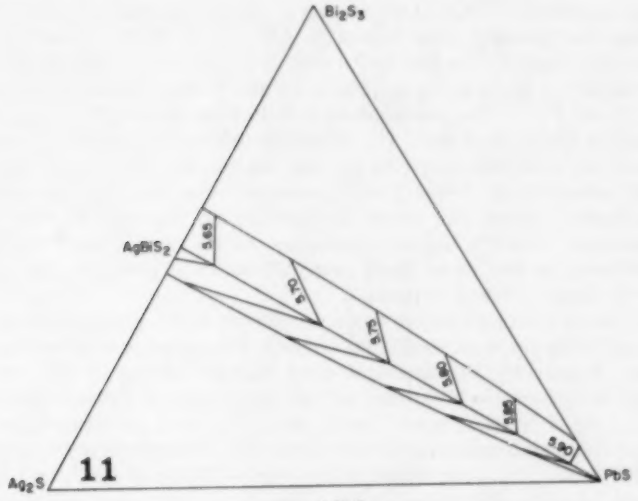
Experimental Results.—The phase diagram (Fig. 12) summarizes the information obtained on the ternary system. In the composition triangle Ag_2S-$AgBiS_2$-PbS, the primary crystallization fields of argentite and galena-

TABLE 5

MEASUREMENTS ON MATILDITE

	Ramdohr (26), on natural material			Graham (11), synthetic product Measured values
	"Corrected" values	Measured values		
$b/2$	3.935	3.91	a	3.918
$a/2$	4.07	4.04	b	4.046
c	5.69	5.65	c	5.662

(It should be noted that Ramdohr's material is a solid solution in equilibrium with a galena phase, whereas Graham's data is on synthetic material without PbS present. This distinction is probably minor, however, as miscibility of PbS in β matildite is very small.)



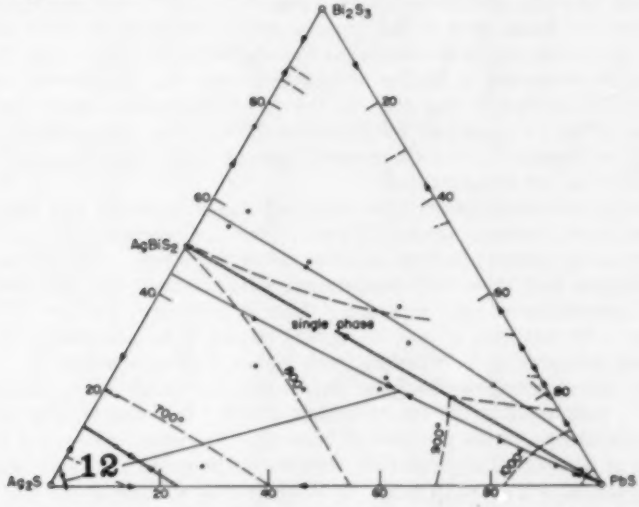


FIG. 11. Cubic lattice parameter of $\alpha AgBiS_2$-PbS ternary solid solutions.
FIG. 12. The system Ag_2S-Bi_2S_3-PbS.

matildite solid solutions are separated by the eutectic boundary curve which has a minimum at 592° C ± 5° at the composition $81Ag_2S$-$5Bi_2S_3$-14PbS. A three-phase tie line connects this minimum point on the boundary curve with minima on the phase boundary of the argentite and galena-matildite solid solutions as shown in Figure 12.

The solubility of Ag_2S at the solidus in the galena-matildite solid solutions decreases continuously from 10 mol % (45 mol % Bi_2S_3, 55 mol % Ag_2S) on the Ag_2S-$AgBiS_2$ side line to 0.4 mol % in the system PbS-Ag_2S whereas the solubility of Bi_2S_3 at the solidus is 16 mol % in AgBiS and decreases to 9 mol % in PbS. The variation in cell dimensions for these ternary solid solutions is shown in Figure 11. Matildite-galena solid solutions containing excess Bi_2S_3 were anisotropic in polished section and showed diffuse, poorly defined reflections in X-ray power patterns. The twinning lamellae found in the $AgBiS_2$ phase with excess Bi_2S_3 were not observed in these ternary compositions. Solid solutions containing excess Ag_2S over $AgBiS_2$-PbS compositions, on the other hand, were all optically isotropic and exhibited relatively sharp diffraction peaks.

Discussion.—The extensive ternary solubility in the galena-matildite structure is probably the most significant feature of the experimental results in this system. Apparently substitutional solid solution of $Ag^{+} + Bi^{+3}$ for $2Pb^{+2}$ need not be quantitatively satisfied at high temperatures, although the addition of excess Ag_2S or Bi_2S_3 must involve some structural accommodation to the resulting charge differences and cation deficiency or excess in order to maintain the cubic form. At lower temperatures the solubility of Ag_2S and Bi_2S_3 in PbS and $\alpha AgBiS_2$ decreases rapidly (Figs. 6, 7) and a similar relationship probably also holds true in the ternary system resulting in solid solutions which are restricted more closely to the $AgBiS_2$-PbS join. The range of these cubic structures is further diminished below the intersection with the $AgBiS_2$-PbS solvus, giving rise to the βmatildite-galena exsolution intergrowths (Fig. 1) described by Ramdohr (*26*). The schematic isothermal sections in Figure 13 gives the general form of phase relations which would be expected at low temperatures.

The experimental results have indicated that schapbacite and schirmerite are not distinct mineral species (Table 1) but are members of a continuous series of solid solutions and are unstable below the solvus. The galena phase is continuous with these high-temperature solid solutions and the assignment of any compositional limit separating them is arbitrary: perhaps PbS solid solutions with less than 10 mol % $AgBiS_2$ should be termed galena, retaining the name schapbacite for minerals with higher $AgBiS_2$ content.

The experimental results have shown that the solubility of argentite in galena is very small in the binary system (0.4%) but may be large, even at low temperatures, in the presence of bismuth. Moreover, silver and bismuth may occur in unequal molecular proportions in the cubic solid solutions without exsolution of a second phase. It is interesting to note in this connection that the argentiferous galena samples from the Freiberg deposit analyzed spectroscopically by Leutwein and Herrmann (*21*) were all richer in Ag_2S than in Bi_2S_3 (Fig. 14). The galena was reported to be homogeneous in polished section and essentially free of elements other than in bismuth and silver.

The solubility of bismuth in galena is similarly dependent on the presence of silver but is perhaps less striking since solubility is appreciable (9%) in

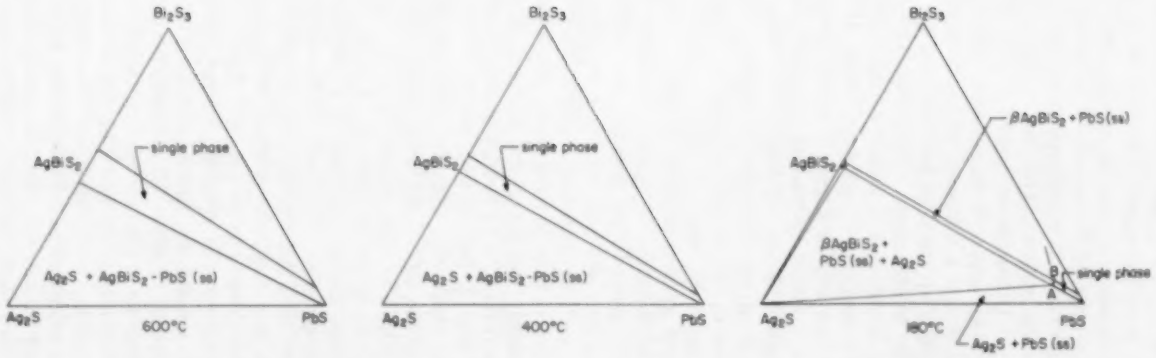


FIG. 13. Subsolidus equilibria for three isothermal sections in the system Ag_2S-Bi_2S_3-PbS.

the binary system PbS-Bi_2S_3. The spectroscopic analyses given by Oftedal (24) of galena samples from Norwegian localities are of interest here since the minerals studied were also reported to contain only bismuth and silver as major impurities. In some of these samples a second anistotropic lead-bismuth sulfosalt was observed in polished section, appearing as lamellae along octahedral directions in the galena. The bulk composition was, therefore, believed to correspond to homogeneous galena formed at higher temperatures. Sample 1 (Fig. 14) appeared in polished section as galena plus a second phase, samples 2, 3, and 4 contained only a trace of the second phase, and compositions 5, 6, and 7 appeared as homogeneous galena without visible exsolution lamellae of the second phase. Assuming 0.1% of a second Ag_2S or Bi-sulfosalt phase can be detected in polished section, these natural galenas can be used to locate the approximate solubility limits at "low-temperature" shown by the cross-hatched area in Figure 4 within the limits of high-temperature solid solutions. These observations compare favorably with the assumed subsolidus relations shown in Figure 13. The analyses of these natural galena samples show no particular tendency for silver and bismuth to combine in equal amounts, i.e., as solid solutions of $AgBiS_2$ in PbS. This variation in the ratio Ag/Bi for trace amounts in galena has lead some investigators to assume that solution of silver in galena has no relation to the presence of bismuth. Goldschmidt (10, p. 407) observed: "Strangely enough, all galena rich in bismuth (about 10,000 ppm Bi) also contains thallium (100–500 ppm) and is always rich in silver, so that it has been suggested that a silver sulphobismuthite such as matildite, $AgBiS_2$, may be substituted for 2PbS. The author considers it to be more likely that silver and bismuth are taken up quite independently into the galena lattice." Chemical analyses of βmatildite-galena intergrowths (26, 5) had led to the opposite view—that solid solution is essentially that of $AgBiS_2$ in PbS and that large excesses of Ag_2S or Bi_2S_3 in galena are not observed. The reason for this difference in opinion can be seen by a study of the 180° C isothermal plane in Figure 13. In any mixture of galena and $\beta AgBiS_2$ with or without a third phase, the composition of the galena must be given by some point along the line *AB*. The isothermal section indicates the general case of a line *AB* that generates a surface with varying temperature. The surface, however, is probably very narrow and may actually be a point in isothermal section and a line in the polythermal model. At any rate, the position of the surface or line will change, but will probably remain on or near the $AgBiS_2$-PbS join, yielding a galena phase in equilibrium with $\beta AgBiS_2$ having essentially a 1:1 ratio of Ag/Bi. On the other hand, the galena samples with trace amounts of silver and bismuth studied by Goldschmidt and others were free of additional ternary phases and there is no restriction on composition within the solubility limits of the single PbS phase. In this case the availability of silver or bismuth exerts the controlling effect on composition independent of the requirements of the phase relationships. Nevertheless, even in trace amounts, one may assume that the presence of silver in galena favors the capture of bismuth (or antimony, etc.) and vice versa, as this would result in a more favorable charge relationship in the structure.

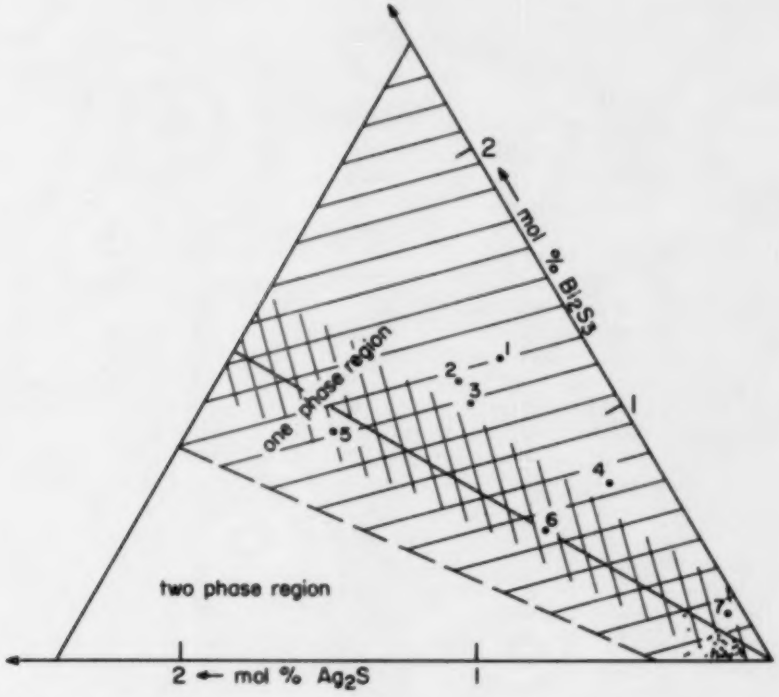


FIG. 14. Ternary composition of some natural galenas (small dots are data from Leutwein and Herrmann, 21; numbered dots from Oftedal, 24. See text for discussion.

Argentiferous varieties of the rare mineral beegerite ($6PbS \cdot Bi_2S_3$) have been reported to contain 10–15 wt. % Ag (27) and have been described as cubic on the basis of morphology. The experimental results indicate that a single cubic phase is stable for beegerite compositions containing more than 3.8 mol % Ag_2S (3.0 wt. % Ag) and that a higher silver content (approaching the $AgBiS_2PbS$ join) would increase the stability of the phase at high temperatures. Below the temperature of the $AgBiS_2$-PbS solvus, "beegerite" containing Ag_2S will unmix into two (galena + Pb-Bi sulfosalt) or three (βmatildite + Pb-Bi sulfosalt + galena) phases, depending on the amount of Ag_2S present. Ramdohr (27) has noted that the only property distinguishing beegerite from galena is the anisotropism. Since anisotropism was also observed in all synthetic galena compositions having excess Bi_2S_3, it seems probable that beegerite is nothing more than a high-temperature galena solid solution. The cubic morphology of beegerite also suggests a single galena phase as originally formed at high temperatures.

SUMMARY

The silver content in many ore deposits has been traced to small amounts of silver minerals in the form of minute inclusions in galena ore. The intergrowths, which are generally disseminated evenly throughout the specimen, have been interpreted as exsolution lamellae resulting from unmixing in the solid state. The most common silver mineral, argentite, however, is only sparingly soluble in galena, and the validity of the interpretation of the inclusions as unmixing intergrowths depended on the discovery of other silver minerals having a greater solubility in the galena structure.

Ramdohr (26) investigated intergrowths of galena and the silver sulfosalt matildite ($AgBiS_2$) and found that matildite is dimorphic, having a high-temperature form isostructural with galena. He proposed that the intergrowths resulted from unmixing of homogeneous solid solutions with falling temperature arising from the sudden decrease in solubility below the inversion temperature in matildite.

Studies of trace elements in galena have shown further that silver and bismuth are very common constituents and that galena rich in bismuth from "high-temperature" ore deposits is almost invariably high in silver (10).

Experimental studies in the ternary system Ag_2S-Bi_2S_3-PbS were undertaken to determine the solubility of Ag_2S and Bi_2S_3 in galena and in ternary solid solutions and to study the effect of the matildite inversion on ternary phase equilibria.

Previous studies of the binary system Ag-S and Pb-S, together with the present experimental results on the system Bi-S, have shown that the three sulfides Ag_2S, Bi_2S_3, and PbS melt congruently in sealed containers at the pressure of the system. Compositional changes due to loss of sulfur to the condensed phases can be minimized by keeping the space above the charge as small as possible. This is especially important in the system Bi-S where congruent melting of Bi_2S_3 occurs at pressures of a few atmospheres. It was concluded that mixtures of these sulfides could be studied as condensed equilibria in sealed containers neglecting the small compositional changes due to sulfur vaporization.

The limiting binary systems Ag_2S-PbS, Ag_2S-Bi_2S_3, PbS-Bi_2S_3, the binary join $AgBiS_2$-PbS, and the ternary system Ag_2S-Bi_2S_3-PbS were investigated using differential thermal analysis combined with quenching methods. The products were examined in polished section and by X-ray diffraction to identify the phases and to determine their limits of solid solution. All samples were sealed in evacuated silica glass tubes to prevent decomposition and oxidation at high temperatures.

The results of the experimental work are summarized in Figure 12. The solubility of PbS in $(Ag_2S)_1$ is 3 mol % at the eutectic temperature (605° C) and that of Bi_2S_3 in $(Ag_2S)_1$ is 4 mol % at the Ag_2S-$AgBiS_2$ eutectic (615° C). Solubility in the high-temperature form ($(Ag_2S)_1$) lowers the inversion in Ag_2S at 590° C to 455° C in the system Ag_2S-PbS and to 522° C in the system Ag_2S-Bi_2S_3. The solubility of PbS in $(Ag_2S)_{11}$ (argentite) is probably less than 1 mol % in both binary systems and in the ternary system also.

Two binary compounds have been synthesized in the system Ag_2S-Bi_2S_3

(Fig. 6). Matildite ($AgBiS_2$) is dimorphic, having a high-temperature galena-type structure (α) that transforms reversibly to a lower symmetry (β) form at 195° C ± 5°. X-ray powder diffraction data on the β modification are compared with previous results on synthetic $\beta AgBiS_2$ (11, 9). The cubic form melts congruently at 801° C ± 5° and is stable over a range of binary compositions. A second binary compound, $Ag_2S \cdot 3Bi_2S_3$, is monoclinic and has no known naturally occurring counterpart.

Miscibility of Ag_2S in PbS is limited to 0.4 mol % Ag_2S in binary compositions whereas significantly higher amounts of Bi_2S_3 (9 mol % at 800° C) may be held in the galena phase in the binary system PbS-Bi_2S_3. Addition of both Ag_2S and Bi_2S_3 to the galena structure, has a profound effect on solubility and a continuous series of solid solutions are formed along the join between PbS and $\alpha AgBiS_2$. The compositional range of the galena phase, moreover, is not restricted to this join at high temperatures, but extends to ternary compositions containing up to 10 mol % Ag_2S or 16 mol % Bi_2S_3 in excess of $AgBiS_2$-PbS mixtures. With decreasing temperature, the stability region of the galena phase decreases, being limited to compositions closer to the $AgBiS_2$-PbS join (Fig. 13). Solid solution is further diminished below intersection with the solvus, related to the structural change in $AgBiS_2$ at 195° C, and gives rise to the unmixing textures observed in matildite-galena intergrowths (Fig. 1). Although the unmixing reflects a large reduction in solid solubility, considerable $AgBiS_2$ remains dissolved in galena at low temperatures. Experimentally, 10 mol % $AgBiS_2$ was found in PbS at 170° C in the presence of excess $AgBiS_2$ and the galena phase in an intergrowth described by Ramdohr (26) contained 8 mol % $AgBiS_2$ (3.76 wt. % Ag, or approximately 1000 troy oz/ton of Ag) as determined using data from the present investigation. It is concluded that the solubility of silver in galena may be extensive, even at low temperatures, when bismuth is present. A similar relationship in the system Ag_2S-Sb_2S_3-PbS is suggested by the available data on miargyrite ($AgSbS_2$) affording a possible explanation for the common occurrence of Ag, Bi, and Sb in natural galenas.

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NATURE AND ORIGIN OF CENTRAL IDAHO BLACKSANDS[1]

C. N. SAVAGE

ABSTRACT

Fifty or more heavy minerals occur in blacksand placers adjacent to the Cretaceous Idaho batholith. They contain niobium (columbium), tantalum, yttrium, zirconium, hafnium, uranium, thorium, titanium, and the rare earths. These minerals are of present or future potential value as sources of metals characterized by versatility, including strength and resistance to heat and chemical corrosion.

Natural concentrations of blacksand involve mineral hardness, texture, chemical composition, and specific gravity; mineral size, shape, and degree of roundness; and major alterations in stream regimen affecting competency, capacity, and interruptions of transportation. The latter include climatic changes, lava damming, crustal warping, faulting, and mass-wasting phenomena. Local deep disintegration of bedrock is an important adjunct to blacksand concentration.

The original source of heavy mineral elements is believed to be Precambrian placer accumulations. These concentrations were later partially dispersed by metasomatic reconversion during diastrophic maxima, and indistinct swarms of accessory minerals were produced. New placers were formed again later through the operation of erosional and depositional agents.

Recent blacksand placers derived their heavy minerals from quartz monzonite, granodiorite, diorite, and metamorphic remnants of original country rock commonly found in adjacent exposures of the Idaho batholith. The batholith may appear deceptively normal in these areas. When present, pegmatite and aplite dikes provide an additional source of heavy detrital minerals. The domination of one or more minerals over others in the more recent placers, appears to be related to the domination of similar elemental constituents in earlier original placer deposits.

Thus recent data on both the petrography of the Idaho batholith and the nature and origin of blacksand placers lead to the following conclusions: erosional processes concentrated the first placer ore deposits in the Precambrian; and subsequent events both geomorphic and metasomatic probably played more important roles in the genesis of all types of ore deposits, including placers, than previously has been supposed.

INTRODUCTION

IMPORTANT placer concentrations of blacksand minerals are located in central Idaho adjacent to the Cretaceous Idaho batholith (Fig. 1). Fifty or more heavy detrital mineral types are known—or have been reported—to be present in these widely distributed deposits. Previously, most of the placer areas were worked for gold, but current interest centers around those localities where detrital minerals contain niobium (columbium), tantalum, yttrium,

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zirconium, hafnium, uranium, thorium, titanium, and the rare earths. These "transition elements" are metals that are not rare but elusive, being widely disseminated in the earth's crust. The minerals that contain these elements, with some exceptions, usually become valuable only through natural placer-type concentration.

Enthusiastically hailed as "space age metals" and "metals of the future," some of the blacksand metals seem to be solving major problems in industry. They are especially useful where strength and resistance to heat and chemical corrosion are of vital importance. Their apparent versatility and variety of applications in their pure form, seems to indicate an assured future market for blacksand metals. One is tempted to comment that they may be to the metal industry what the "miracle drugs" were to medicine.

FIG. 1.

Scientists have been investigating problems related to the origin, location, and use of blacksand placer minerals for several years. The results of these studies are available in many publications. In turn, the growing importance of the blacksand metals is well-reflected by this literature.

Idaho placers may be separated into five or more categories on the basis of dominant mineral types. Some deposits contain high percentages of monazite, ilmenite, magnetite, uranothorite, thorite, columbite, or tantalite. Columbite and tantalite may occur with uranothorite and thorite minerals in economically valuable deposits. The latter are mostly intimately associated with roof pendants or metasedimentary rocks within the batholith. Zirconium and hafnium appear to be universally present in all placer deposits.

NATURAL CONCENTRATION OF MINERALS

Natural concentration of detrital minerals is aided or hindered by many physical phenomena. Among these are: mineral characteristics such as hardness, texture, chemical composition, and specific gravity. There are definite relationships between mineral hardness, density, and occurrence in specific suites. Detrital minerals of similar hardnesses and/or similar densities tend to occur together; where one is found others in a specific suite may be present also (Table 1).

Mineral size, shape, and degree of roundness are additional factors that are involved in the mechanics of placer accumulation. These physical characteristics affect concentration of blacksands during their transportation and deposition phases.

Perhaps the most obvious reason for heavy mineral concentration is proper physical setting. In Idaho, certain events in geologic history have produced important drainage derangements which, where proper source rocks are available, may cause blacksand placers to accumulate. Among the causes of variations in stream regimen are: climatic changes, including glaciation; lava damming; crustal warping; faulting; and landslide phenomena.

Local depositional sites produced by the above phenomena, may be found by identifying such geologic features as: centripetal stream patterns occurring around a basin containing a swampy meadow or piedmont plain; fan and delta-like deposits, and evidence of temporary ponding; high terraces or "benches"; evidence of stream rejuvenation, and changes in base level; and evidence of drainage reversal, including stream piracy, barbed tributaries, and swampy flats along drainage divides. These phenomena occur extensively, but they are not always indicative of valuable placer deposits. Most Idaho placers are trapped types, of stream and glaciofluvial origin. Some of the smaller deposits of columbium and tantalum appear to be transitory placers of gravity and eluvial types (Table 2).

Finally, it should be noted that the competency and capacity of natural transporting agents, and the availability of natural sedimentary traps developed as a result of the above mentioned geologic history, are extremely important influences in placer accumulation. Idaho's early tectonic and more recent

TABLE 1

MINERAL HARDNESS AND WEIGHT ANALYSIS IDAHO PLACER MINERALS

Relative specific gravity		Soft	Hardness Intermediate	Hard, to very hard
	Light	mica	nepheline, leucite, sodalite[1]	quartz, feldspar
	Heavy	(none)	apatite amphibole anatase, ilmenite, sphene allanite[3] cyrtolite pyrochlore	olivine pyroxene garnet, tourmaline silimanite, corundum, topaz zircon
	Very heavy	cinnabar silver gold	microlite, hjelmite fergusonite,[3] formanite euxenite, polycrase eschynite, priorite betafite, brannerite, samarskite[3] xenotime, monazite uranothorite hematite platinum	columbite*[4], tantalite* baddeleyite*, rutile cassiterite magnetite, pyrite

[1] Minerals listed in same horizontal line in a single column have general chemical or physical similarity.

[2] Minerals underscored with broken line may be radioactive or not depends upon presence or absence of actinide elements, e.g. minor quantities (---.)

[3] Minerals underlined are generally radioactive, e.g. actinide elements are contained in major proportions (—).

[4] Minerals that are not radioactive except when intergrowths of radioactive minerals are present, indicated by asterisk (*).

geomorphic history have played an important role in both preparation of sedimentary traps and subsequent entrapment of detrital blacksands.

ORIGINAL SOURCE OF HEAVY MINERAL ELEMENTS

Metasomatic action during and after emplacement of the Idaho batholith produced vague streaks of mineral differentiates within the bedrock. Whether one accepts an orthomagmatic or a metasomatic concept of batholith origin, it is a fact that the normal accessory minerals were augmented by additional differentiates. The latter must have resulted from an over-abundance of some of their constituent elements. These elements probably were derived at various places from local sources in the country rock during batholith emplacement.

The present northern and western boundaries of the deroofed Idaho batholith appear to be located near the original sites of Precambrian axes of uplift. These same areas coincide well with probable axes of orogeny and igneous activity during the latter part of the Mesozoic era. It is believed that blacksand minerals accumulated and were concentrated in ancient placers

TABLE 2

PLACER CLASSIFICATION

I. *Residual Placer:* forms where mechanical and chemical weathering remove some of the softer and more soluble minerals; settling in place later produces an initial concentration of heavy minerals.

II. *Transitory:* forms where heavy minerals are briefly halted in process of moving from points of residual accumulation into a semi-mobile environment; the latter is governed partially by the influence of slope wash and by gravity (mass-wasting).

(a) *Eluvial-type placer:* forms where frost-heaving and slope wash combined to remove some of the lighter minerals.
(b) *Gravity-type placer:* occurs where there is some concentration of the more dense minerals through gravity; includes soil creep, mud flow, slides, rock fall.

III. *Trapped Placer:* the more familiar type placer that forms when mobile agents concentrate heavy minerals as a result of some sedimentary trap; the minerals are immobile, but the period of immobility varies greatly.

(a) *"Bahada" fan-type placer:* dry environment, fan or cone, built chiefly by intermittent stream flow.
(b) *"Pluvial" fan-type placer:* wet environment fan or cone, built by stream flow.
(c) *Stream bed-, bar-, terrace-* or *"bench" placer:* built along an ancient or recent stream bed by the usual stream action and changes in its regimen.
(d) *Glacio-fluviatile bed-, bar-,* or *terrace-placer:* placer built chiefly by glacial meltwater stream.
(e) *Eolian placer:* heavy minerals are concentrated by the winnowing action of the wind.
(f) *Beach- or elevated strandline-placer:* built by concentration of minerals as a result of wave and shore current action; placer may be of either lacustrine or marine origin.

that flanked upland areas. Later emplacement of igneous rocks partially dispersed the placer concentrates, and the latter provided elements with which indistinct vein-like swarms of mineral differentiates were formed. Beginning with the original crust, such a sequence may have been repeated more than once in the following order:

(1) placer concentration of heavy minerals derived from local bedrock sources;
(2) partial dispersal and metasomatic reconversion of the heavy mineral elements into accessory minerals and mineral swarms during diastrophic maxima;
(3) development of new placers through the operation of erosional and depositional agents.

This hypothesis of metasomatic reconversion through geologic time may explain concentration of heavy minerals in the earth's crust along belts of persistent diastrophism. Certain special physical conditions existing locally during stage two above, might result in the emplacement of economically valuable lode minerals where sufficiently rich concentrations of the proper elements were present in the country rock. Metasomatism may be more closely related to the genesis of all types of economic mineral deposits than heretofore suspected (Fig. 2).

There seems to be no doubt that the domination of one mineral over others depends upon the predominance of one of three types of bedrock environment and relative abundance of specific original elemental mineral constituents.

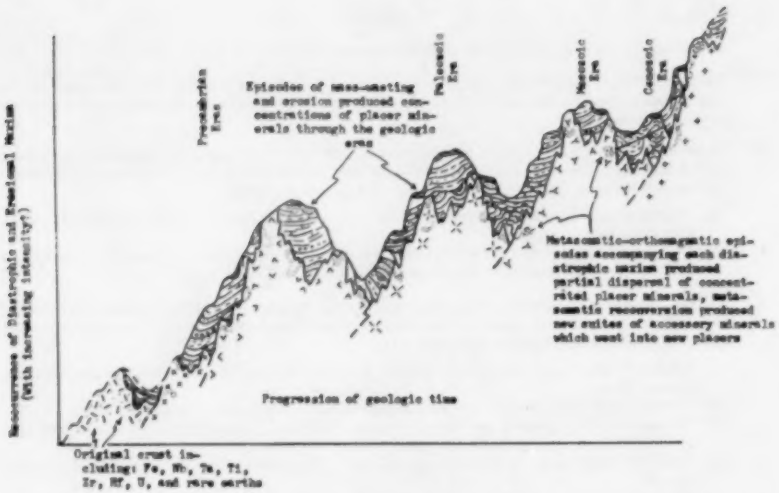
Precambrian Era
Episodes of mass-wasting and erosion produced concentrations of placer minerals through the geologic eras
Paleozoic Era
Mesozoic Era
Cenozoic Era
Metasomatic-orthomagmatic episodes accompanying each diastrophic maxima produced partial dispersal of concentrated placer minerals, metasomatic reconversion produced new suites of accessory minerals which went into new placers
Progression of geologic time
Original crust including: Fe, Mn, Ta, Ti, Zr, Hf, U, and rare earths

FIG. 2. Metasomatic reconversion or regeneration and reconcentration of detrital minerals (diagrammatic representation).

For example, magnetite, monazite, ilmenite, and zircon (with hafnium) are more common in placers where the bedrock contains streaky concentrations of accessory minerals in addition to the normally dispersed accessories. Euxenite, samarskite, brannerite, columbite, and tantalite may dominate over other placer heavy minerals where pegmatite and aplite dikes are abundant locally. Uranothorite, thorite, tantalite, and columbite may occur with some abundance in areas where roof pendants are present in the batholith.

Geologic data assembled in the following reports by the U. S. Geological Survey provide strong support for some of the above conclusions: Bulletin 1074-B, a summary report covering work on radioactive minerals in the states of Washington, Idaho, and Montana from 1952 to 1955; Bulletin 1082-A, containing conclusions of J. B. Mertie, Jr., relative to his work with the coastal plain placers in the eastern United States and an open file report by D. L. Schmidt on the petrography of the Idaho batholith in Valley County, Idaho. There are other equally important sources of information that have led to some of the conclusions herein stated, including recent field work by members of the Idaho Bureau of Mines and Geology.

IMMEDIATE SOURCE OF PLACER MINERALS

All the important blacksand placers in Idaho occur adjacent to certain undefined contacts between different types of rock composing the batholith and associated metamorphic rock. Quartz monzonite, granodiorite, diorite, and metamorphic remnants of original country rock are common in such in-

distinct contact zones. Detrital minerals such as monazite and ilmenite, for example, may occur abundantly in recent placers where the above-mentioned, vaguely banded mineral differentiates occur in the bedrock. Megascopically, such differentiates are not distinguishable and the rock of the batholith may appear deceptively normal with uniform distribution of accessory minerals.

The presence of these additional sources of accessory minerals was early suspected during blacksand field investigations; later, several reports on petrographic aspects of portions of the batholith tended to verify earlier supposition. For example, recent concentrations of monazite may be found adjacent to highly disintegrated bedrock at outcrops at several localities. After discovery of a few of these small local accumulations, others may be found by spotting a suitable trap, and crossing the area with a portable scintillometer.

Less commonly, blacksand placers occur where pegmatite and aplite dikes are plentiful. These intrusives may yield an additional supply of accessory minerals. It is interesting to note that while known columbite-tantalite placers occur in such areas, local pegmatite dikes and float rock show little of the coarse mineral material that may be present in the placer nearby. Since the type of minerals with which we are concerned is known to occur in pegmatites in other regions, it is safe to assume that pegmatite dikes adjacent to Idaho placer areas should be sources of detrital minerals in local placers.

The decayed and disintegrated bedrock that occurs in most Idaho placer areas is well prepared for natural winnowing. Effects of jointing, shearing, shattering, and hydration are prominently displayed. Many placer areas are associated with actual or inferred fault zones and hot springs are common in the same localities. The latter may have had a part in developing deep rock disintegration. Placer concentration from once more extensive decayed bedrock in these areas is believed to have occurred in a relatively short time, for example, during the late Pleistocene and Recent. These more recent placers in central Idaho have current or future economic potential.

CONCLUSIONS

If it is assumed that originally the elements were dispersed laterally with some uniformity in the earth's crust, the uniform distributions may have been limited vertically to successive concentric layers. The density of the latter would tend to increase somewhat toward the earth's center. If there is truth in the original premise of laterally uniform distribution of elements, then the emplacement of massive ore deposits and the accumulation of placer minerals represent concentration of originally widely dispersed elements. The development of mineral deposits of commercial value is the result of geologic processes that have concentrated minerals and their elements in relatively small portions of the earth's crust. The erosional process must have played an important role in the genesis of the first ore deposits that accumulated as heavy mineral placers in the Precambrian.

Through the ages, geological forces may have been responsible for a semi-rhythmic sequence of events, for example, alternately concentrating and par-

tially dispersing the elements and their related minerals within and on the earth. These processes involved some of the elements that are more susceptible to lode mineral concentration during periods of maximum crustal unrest, and emplacement of igneous rocks; and other elements and minerals were involved that, like the Idaho blacksand placers, are more susceptible to placer concentration. Recent work on the nature of the detrital minerals and their origin in Idaho may have provided information that will be of assistance in solving some of the many problems related to ore genesis.

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A GEOCHEMICAL INVESTIGATION OF THE ATHABASCA BITUMINOUS SANDS[1]

J. B. F. CHAMPLIN AND H. N. DUNNING

ABSTRACT

The Athabasca bituminous sands, Canada's largest petroleum reserve, lie in Northern Alberta where they outcrop along the headwaters of the Athabasca river. The accessibility that makes it possible to exploit the formation by mining also permits study of the interrelationships of the asphaltic oil, reservoir materials, and the geochemically significant porphyrin materials.

The metal-porphyrin and porphyrin aggregate contents of the Athabasca oil fractions were determined quantitatively. These fractions also were further subdivided by alcohol extraction and extensive chromatography. The metal-porphyrin contents of these fractions corroborated the bulk analyses and revealed the presence of a nickel-porphyrin complex in addition to the previously established predominant vanadium-porphyrin complex.

The Athabasca oil is similar to other asphaltic oils, of high vanadium content, in porphyrin and metal contents as well as in many of its bulk properties. Correlations of the geochemical and petrological data indicate that the bulk of the Athabasca oil has had a sheltered existence; one relatively free of weathering influences. Identification of the nickel-porphyrin complex with larger amounts of the vanadium-nickel complex is another indication of the similarity of this oil to other vanadium-rich oils.

INTRODUCTION

THE Athabasca bituminous sands, Canada's largest petroleum reserve, lie in northern Alberta along the headwaters of the Athabasca River. Here, some 200 miles northeast of Edmonton, the widespread Devonian limestone outcrops along the river banks for many miles as it dips gently to the southwest into the Alberta basin. The Athabasca bituminous sand overlying this dense limestone is a basal Cretaceous unconsolidated sand formation almost entirely uncemented except for the bitumen with which it is saturated. This formation outcrops in an area some 80 by 240 miles around the settlement of Fort McMurray; hence the more proper geologic name, the McMurray formation. Although this lower Cretaceous formation lies unconformably on the Devonian limestone, it follows the regional dip to the southwest and, according to Sproule (13), is believed to have had its origin in a Paleozoic quartzose sandstone to the east known as the Athabasca formation. This reservoir recently has received widespread interest because of the proposed use of an atomic explosion to facilitate recovery of its bitumen content.

[1] From the Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla. Presented as part of the symposium "Chemical Aspects of the Origin, Migration, and Accumulation of Oil," at the 134th National Meeting, American Chemical Society, Chicago, Ill., September 7–12, 1958.

The accessibility that makes it possible to exploit the formation economically by mining also permits study of the interrelationships of the asphaltic oil, reservoir materials, and porphyrin distribution in the reservoir. Recent investigations of the porphyrin content of crude oils by Dunning and Moore (5) have shown that these complex residues of chlorophyll or hemoglobin may provide information on the genesis and migration of petroleum. Accordingly, a geochemical study has been made of these sands and the bitumen they contain.

EXPERIMENTAL PROCEDURES AND RESULTS

Investigation of the Athabasca oil was begun by extraction of the bitumen from the sand by a series of solvents, used in order of increasing polarity. The oil sand was placed in a Soxhlet extractor and successively extracted by hexane, iso-octane (2,2,4-trimethyl pentane), iso-octene (2,4,4-trimethyl pentene), benzene, a benzene-ethanol azeotrope, and pyridine.

The freshly mined oil sand from the Abasand quarry was compared to a sample of oil sand taken from the Bitumount quarry several years ago and kept bottled under air. The distribution of the Athacasca oil fractions obtained by the successive solvent extractions described above is shown in Table 1.

Although both samples contained about 16 percent oil by weight, the results show a distinct difference in their extraction. The oil of the aged Bitumount sample is extracted from the sand less extensively by these solvents than is the oil from the fresh Abasand sample. Clark (1) shows only minor differences in random samples taken from these two areas. Therefore, aging and contact with air probably are important factors in making the oil less readily extractable by aliphatic hydrocarbons. The values shown in Table 1 undoubtedly include the effects of desorption processes, for 85 percent of the whole Athabasca oil is soluble in hexane.

The extracts of the bituminous sands were subjected to further study by extraction and chromatography. They first were separated into ethanol-soluble and ethanol-insoluble portions in a continuous alcohol extractor. The alcohol-soluble portions were then chromatographed on columns of partly deactivated alumina. This alumina was prepared by moistening Alcoa F-20 and drying it thoroughly in an oven at 50° C. The alumina that would pass

TABLE 1

WEIGHT-PERCENT OF OIL OBTAINED BY SUCCESSIVE EXTRACTIONS FROM OIL SAND

	Aged Bitumount sample		Fresh Abasand sample	
	Successive	Cumulative	Successive	Cumulative
Hexane	64.5	64.5	76.9	76.9
Iso-octane	6.4	70.9	1.5	78.4
Iso-octene	4.1	75.0	3.0	81.4
Benzene	18.2	93.2	15.1	96.5
Benzene-ethanol	4.2	97.4	3.2	99.7
Pyridine	2.6	100.0	0.3	100.0

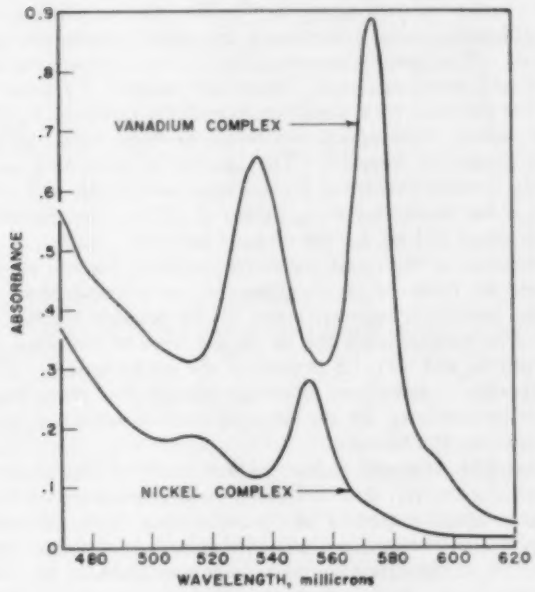

Figure 1.–Spectra of metal-porphyrin complexes from the Athabasca oil.
(Vanadium = 0.057 wt. percent in benzene)
(Nickel = 0.14 " " " ")

FIG. 1.

through a 40-mesh screen then was added to a column with continuous tamping and the column prewet with hexane before adding the fraction to be chromatographed.

The samples were dissolved in hexane after peptizing with a few drops of benzene. Once the sample solution had been added to the column, development was begun with hexane, continued with increasing percentages of benzene in the hexane eluent, then with low percentages of isopropanol in benzene, and completed with a solution of 30 percent isopropanol in benzene. The chromatographic fractions and the whole alcohol extracts were analyzed spectrophotometrically in benzene solutions for metal-porphyrin complex content. The relative concentrations of these complexes were determined from the increase in absorbance above the "background" for the major absorption peaks in the visible wavelengths. Actual concentrations were then calculated using a molar extinction coefficient of 3.4×10^4. This value recently was established for the synthetic vanadium complex of mesoporphyrin IX dimethyl ester by Moore (10). The extinction coefficient of the nickel-porphyrin complex has not been determined recently but was reported to be 3.4×10^4 by Stern (14).

The vanadium-porphyrin complex was identified as the major porphyrin component although lesser amounts of the nickel-porphyrin complex also were identified. The spectral identifications of these complexes were verified by porphyrin and metal analyses. Scott and others (11) have qualitatively determined the presence of a vanadium-porphyrin complex in Athabasca oil extracts. However, there appears to be no previous report of the presence of the nickel-porphyrin complex. The spectra of these two complexes derived from the hexane extract of the oil sand are shown in Figure 1. The major peaks in the visible wavelengths are at 573 mμ for the vanadium-porphyrin complex and 553 mμ for the nickel-porphyrin complex.

The distribution of the metal-porphyrin complexes in the various extracts is summarized in Table 2. A significantly low percentage of less than 2 percent of the porphyrin recovered was in the benzene fraction, 15 percent of the total oil by weight, while the iso-octane fraction contained 6 percent of the total porphyrin and only 1.5 percent of the oil by weight. The sequence of solvents appears to have been thorough enough that there was little porphyrin left to be extracted by the benzene-ethanol azeotrope, pyridine, and indeed very little by the benzene.

Chromatographic analyses of the solvent fractions also concentrated the nickel-porphyrin complex into detectable and measurable amounts. The metal-porphyrin complex content of the Athabasca crude oil determined by chromatography substantiated the values obtained from the alcohol extracts. The spectral data of the metal complexes are corroborated by porphyrin aggregate determinations which indicated a porphyrin content of 260 p.p.m.

In Table 3, five asphaltic oils obtained from widely separated locations are compared as to relative contents of porphyrin aggregate and trace metals. These oils are the Athabasca from northern Alberta; the Santa Maria Valley from the California coast; the North Belridge from the upper San Joaquin

TABLE 2

DISTRIBUTION OF PORPHYRIN MATERIALS IN FRESH ATHABASCA OIL SAND EXTRACTS

	Concentration, p.p.m.		Percent of total
	In total extract	In whole oil[a]	
Vanadium-porphyrin complex			
Alcohol-soluble portion of:			
Hexane extract	250	190	73.0
Iso-octane extract	1,060	16	6.2
Iso-octene extract	405	12	4.6
Benzene extract	20	3	1.2
Benzene-ethanol extract	25	1	0.4
Pyridine extract	0	0	0.0
Total		222	85.4
Nickel-porphyrin complex			
Total	—	30	12.0
Porphyrin aggregate	—	260	100.0

[a] 68 percent of the whole oil is alcohol soluble.

TABLE 3

PORPHYRIN AND TRACE METAL CONTENTS OF CERTAIN ASPHALTIC OILS

	Tatums[1]	Athabasca	S.M. Valley	N. Belridge[2]	Coleville
Geologic age of reservoir	Penn.	L. Cretaceous	M. Miocene	Pleistocene	L. Cretaceous
Vanadium (p.p.m.)	110	180	280[3]	23	94
Nickel (p.p.m.)	55	80	130[3]	83	32
$\frac{\text{Vanadium}}{\text{Nickel}}$ (mole ratio)	2.3	2.6	2.5	0.3	3.4
Porphyrin aggregate (p.p.m.)	165	260	300	390	110
$\frac{\text{Total V + Ni}}{\text{Total porphyrin}}$ (mole ratio)	9.1	9.0	12.2	2.3	10.4

[1] Moore (10).
[2] Skinner (12).
[3] Dunning (6).

Valley of California; a midcontinent oil from the Tatum's field in southwestern Oklahoma; and Coleville, from Saskatchewan, Canada.

The Athabasca oil seems quite similar to the other high-vanadium oils. About one-tenth enough porphyrin is present to complex all of the vanadium and nickel present. It is notably different from the North Belridge sample which is unusual in containing the nickel complex as the major porphyrin component and in containing half enough porphyrin to complex the nickel and vanadium present. The similarity of the Athabasca oil, in vanadium, nickel and porphyrin contents, to other high-vanadium, asphaltic oils is illustrated in Figure 2.

The sand recovered after removal of the oil by solvents was fine grained with few large particles or pebbles. The cumulative frequency curve of the particle size distribution is shown in Figure 3. This illustration compares the Athabasca sand curve to curves representative of types of sedimentary sand deposition. Comparison of the curves shows that the Athabasca apparently is a combination of beach and dune sands. Calculations of the overall sorting factor (So) and the sorting relative to the median diameter (Sk) as discussed by Twenhofel (15) largely confirm this conclusion. The sand is predominantly rounded quartz grains with a high percentage of these frosted, characteristic of windblown sands. In minor quantities are the minerals feldspar, muscovite, garnet, tourmaline, and a few others. The tourmaline is especially notable in that the relative content increases sharply in the particle sizes under 50 microns. Although the clay minerals seemed to be markedly absent in all samples, X-ray analysis of the fine fractions indicated that the clays may be present in low concentration.

In all the size ranges, a large percentage of the sand grains are actually ovoid pellets. Although opaque in the larger sizes, these pellets may be identified as flattened balls of powdered quartz, not clay, cemented together by a dark amber amorphous material that appears to be an organic residue. This was characteristic of all the pellets studied. The pellets seemed to be

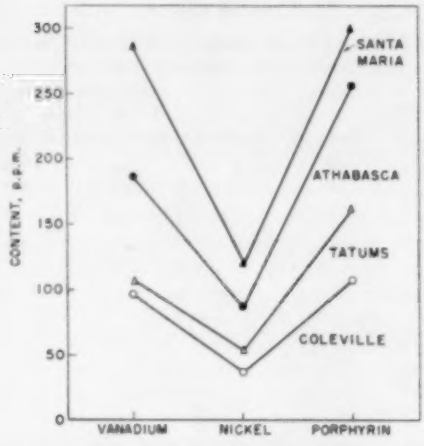

Figure 2.- Metal and porphyrin contents of some asphaltic oils.

FIG. 2.

composed of quartz particles about the size range found in loess. Whereas this requires a high degree of grading by the depositional process, the sand formation as a whole is poorly graded generally, with considerable cross

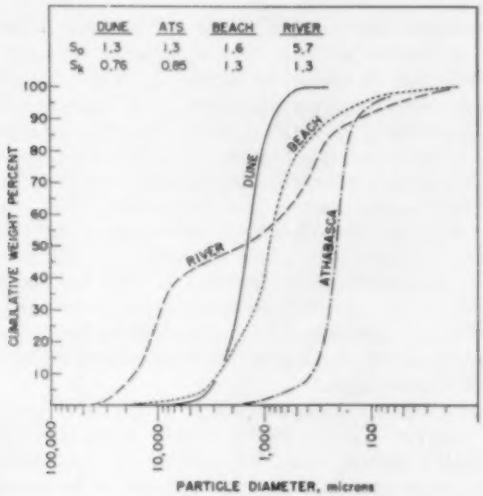

FIG. 3.

bedding. Kidd (8) reported areas of clean sands interfingering with the oil sands while, according to Hume (7), coring in some areas has suggested the existence of large layers of bitumen, relatively free of sand.

DISCUSSION

The high porphyrin content of the major portion of the Athabasca oil indicates that the bulk of the oil has not been subjected to extensive weathering. The relatively high asphaltic content and other bulk properties of the oil appear to substantiate the results of the porphyrin studies. This would be in accord with the conclusions of Scott (11) and Montgomery (9). The fact that the Athabasca oil is a very asphaltic one would, according to Corbett (4), argue for the oil being a young, immature oil arrested in its development by shallow burial. Physical and chemical characteristics of the Athabasca oil pointed out by Montgomery (9) show strong similarities to other Cretaceous oils of Canada and strong dissimilarities to the Devonian oil. Montgomery's work (9) and the data regarding porphyrin content established here indicate the bulk of the oil has had a rather sheltered existence; one relatively free of weathering influences. Identification of small amounts of the nickel-porphyrin complex with larger amounts of the vanadium-porphyrin complex is another indication of the similarity of this oil to other vanadium-rich oils.

The vanadium- and nickel-porphyrin complexes are quite stable in crude oils in the absence of air as shown by the periods for which they have persisted underground and by laboratory observation. However, they may be expected to undergo considerable decomposition on the weathering of a crude oil in view of the ease of decomposition of these substances in benzene on exposure to air and light. Constantinides (2, 3) was able to show these complexes were very subject to decomposition during air blowing of bitumens over a relatively short period of time. Natural weathering processes could therefore be expected to cause a loss of volatile components and a reduction in the porphyrin content by oxidation. This oxidation process would increase the ratio of vanadium and nickel to the porphyrin present in the oil. No marked difference in this ratio was observed between Athabasca oil and the other asphaltic oils shown in Figure 2.

Therefore, it may be concluded that the correlations of the vanadium, nickel, and porphyrin contents of the Athabasca oil and other asphaltic oils, which are unweathered, indicate that the Athabasca oil has not been subjected to extensive weathering despite its present thin overburden.

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P.O. Box 1321,
BARTLESVILLE, OKLAHOMA,
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CRITICAL REMARKS ON THE GENESIS OF ORE AS APPLIED TO FUTURE MINERAL EXPLORATION

RENO H. SALES

ABSTRACT

The syngenetic, metamorphic water, and source bed concept theories of ore deposition proposed by Anton Gray, C. L. Knight and others, to explain ores in sedimentary rocks, are challenged on the basis of a survey of the literature and personal observation. A hydrothermal origin for the Northern Rhodesian Copperbelt deposits is indicated by the presence of post-Roan age igneous rocks and post-gabbro mineralization, the wide distribution of ore in the various Lower Roan lithologic types, and the zoning of the copper-iron sulfide minerals and minor elements.

The proposal by Gray and Knight that igneous rocks are not favorable as guides to nonferrous metal deposits, and Gray's hypothesis that the redistribution of connate waters and their dissolved metals by metamorphic processes was responsible for the emplacement of ores, are rejected as contrary to field evidence. The absence of exposed potential igneous source rocks is shown to be an invalid argument for the proponents of any syngenetic hypothesis. The common association of ore deposits with calc-alkaline intrusive rocks and their derivatives is, however, demonstrated to be convincing evidence that an exploration program based upon a magmatic theory of origin, would have found most of the important known nonferrous metal deposits of the world. It is urged that prospecting be continued on the sound basis of accumulated knowledge of the lithologic and structural facts surrounding known ore deposits.

SEVERAL geologists in recent years have expressed opinions that many ore deposits in sedimentary rocks are syngenetic. Some of the deposits mentioned are large and important producers, such as the Tri-State district, the copper deposits of Northern Rhodesia, the Rand of South Africa, the White Pine district in Michigan, the zinc deposits of upper Silesia, and Broken Hill, Australia, to name only a few. Among those contending for a "syngenetic" or a "metamorphic water" origin for ores in sedimentary beds are Anton Gray (12) and C. L. Knight (16). For the Northern Rhodesian copper ores, W. G. Garlick (10) and G. R. Davis (6) conclude they are syngenetic after extensive and careful studies of the Roan Antelope and other mines. A number of geologists including Knight and C. J. Sullivan (18) have apparently accepted the Garlick and Davis theory as applicable to all of the copper deposits of the Northern Rhodesia area. After reading these articles I must conclude that the theories of "syngenetic" and "metamorphic water" origin rest mainly on two claims; (1) that there are no visible granites or other igneous rocks in the vicinity of the deposits from which hydrothermal ore-bearing fluids could have been derived; and (2) in the absence of an igneous source the ores must be syngenetic with the host rock. More recently Gray

modified the syngenetic theory by proposing that the ore may be "epigenetic" to the host rock, but that the ore metals have been dissolved by metamorphic waters from either the host rock or nearby sediments and transported to the place of deposition. Gray argues against the theory that granite and granitic magmas are sources for deposits of copper, zinc, and lead.

There is an increasing realization by mining and exploration companies that a knowledge of the genesis of ore deposits is an important qualification for field geologists carrying on the search for ores. Because of this fact the present writer is disturbed at the length to which Gray and Knight have gone in minimizing the importance of igneous activity in the formation of ore deposits. Therefore, I feel compelled to comment critically on the generalized statements made by Gray (12) in his Wernher Memorial lecture. I shall also add some specific observations concerning the Northern Rhodesia copper deposits, frequently referred to in the literature as deposits of syngenetic origin.

In a recent article, C. L. Knight (16) made the statement that prior to 1950 he had become "dissatisfied with the popular theory—that the majority of ore bodies had a magmatic origin and developed by a process of fractionation from the magma—*largely because the theory was of no use in the practical business of finding new orebodies.*" (Italics by present writer.) Such a statement hardly deserves comment. Dr. George Schwartz, (17) in a recent issue of ECONOMIC GEOLOGY, has effectively answered Knight by listing nineteen examples of important ore deposits found in sedimentary rocks where there has been general agreement that they are of magmatic origin. In these cases and countless others the theory of magmatic origin paid off handsomely to the prospector.

Like Gray, Knight realizes that the syngenetic theory has one important weakness, namely, that the ore constituents are not depositional syngenetically in their present position and textural relationships in sedimentary rocks. They have "migrated," as Knight puts it, from their original site of syngenetic deposition. Therefore, to by-pass any explanations of where the minerals came from originally, what the transporting medium was that moved them from source points to places of deposition, and other unsolved problems involved in the syngenetic theory, Knight conveniently generalizes his idea as the "source bed concept." Gray, recognizing the tremendously important part played by water as a medium of transport of the metals of ore deposits from source to where they are now found, and having noted the absence of granite in a few examples, comes up with the "metamorphic water" theory as opposed to hydrothermal solutions derived from magmas. Attention must be drawn to the fact that if the ore constituents have migrated under any chemical or physical gradient, the argument of impenetrability of sedimentary host beds ceases to apply only to theories of igneous sources for ore minerals.

Turning now to his lecture, "The Future of Mineral Exploration," Gray appears to have leanings toward the syngenetic theory now being advocated by some geologists to explain certain types of ore deposits. He seems willing to accept the idea that when an ore deposit occurs in a sedimentary formation where no igneous rocks can be seen in the immediate vicinity, the deposit is

probably syngenetic, that is, it is formed through the agency of waters unrelated to igneous activity. But, in the absence of granite or other igneous intrusives to supply ore solutions Gray substitutes "metamorphic" water which is chiefly connate water, or possibly meteoric water, activated by metamorphism accompanying earth processes such as mountain building.

In one respect, however, Gray's "metamorphic water" theory is more epigenetic than syngenetic, inasmuch as under his theory the ore constituents of a deposit are not necessarily syngenetic with, or derived from, the sedimentary bed in which the ore deposit occurs. In the truly syngenetic copper sulfide deposit in a sedimentary formation for example, the copper and sulfur are deposited contemporaneously with the other mineral constituents which make up the host rock, whereas under the Gray "metamorphic water" theory the ore minerals are introduced after the host rock is formed. To quote from page 26 of Gray's printed lecture:

> In the first place these concentrations of metals may be, and are, found in all kinds of rock, igneous, sedimentary and metamorphic. Some were undoubtedly formed during, and by the processes of, the formation of the rock itself, as the gold and tin in alluvials, the oolitic iron ores in sedimentary formations and the platinum and chromite in igneous rocks. Others, like certain nickel ores and bauxites, are residual. But with the exception of these sedimentary, igneous and residual concentrations, the deposits from which our metals are recovered, veins, mantos, stockworks, porphyry coppers, limestone replacements, copper and uranium in sandstone, contain minerals which were introduced into openings in the rocks long after those rocks were formed. Nearly all geologists agree that the materials of these minerals were carried by, and the minerals deposited in, water.

Eliminating the word "long," geologists will not find much fault with that statement. The important question is, what was the source of the transporting ore solution? Upon this vital question there is diversity of opinion, but all is not "chaos" as suggested by Gray. The present writer will agree that the literature embracing the science of ore deposits may well reach a chaotic state if flooded by factually unsupported theories and generalizations on the origin of ores.

Gray says:

> Nevertheless, one theory is dominant today: that the metals and some of the water came from a deeply buried molten rock material called magma which on solidification produced igneous rock. Since granitic magmas are commonly supposed to be the particular source of most metals it is contended that ore deposits should be looked for in association with granites. That is the theory generally offered as a guide to exploration.

Never within my knowledge has it been contended by the proponents of the magmatic theory that we should look only to granites for ore deposits. I need only to note the association of nickel-copper ores with norite at Sudbury and the many important ore deposits the world over (14) genetically related to basic rocks. Surely, no experienced geologist at the head of a mining exploration company would instruct his field men to concentrate their efforts solely on areas of granite, or on sedimentary rocks, no matter what metal is being sought.

In support of his idea that granites would not serve as a guide to ore, Gray names some important mining districts where the ore bodies are "not only in sedimentary rocks, but in some of these fields there is not a granite exposed for miles around." The absence of outcrops is no proof of the non-existence of granite in the earth beneath the ore producing districts. According to most students of igneous rocks a granitic magma, in its upward invasion of roof rocks, solidifies before approaching within thousands of feet of the then existing surface. In view of this fact, exposures of granites at the surface will depend upon depth of erosion, or possibly upon a combination of faulting and erosion. In any event, we may be sure that there are many unexposed granites, granite cupolas, bosses, or plugs, whose tops are at various depths below the surface and, no doubt, under important ore producing districts, hidden because they have not yet been uncovered. The later the granite invasion the less the chance of it being exposed through erosional processes. In areas where topographic relief is small, the presence of sub-surface granite may be indicated by contact effects, or by intrusions of aplite, granite-porphyry, quartz-porphyry, rhyolite, or basic dikes; all derivatives of granitic magmas.

The present writer earnestly advocates the theory that from the "ore search" point of view, granitic rocks are attractive as clues or leads to ore deposits, but this statement must not be understood as advancing the idea that the presence of granite always means a nearby ore deposit. Bodies of granite intruding gneisses, schists, and almost every type and age of sedimentary rock showing little or no indications of ore within the invading granite or in the enclosing rocks are not uncommon. This is to be expected from the very nature of the geologic processes involved as the granitic magma "eats" its way upward through the rocks in its path of advance. Unless the emplacement and cooling of the magma are disturbed at critical times by such events as faulting, fissuring, or dike intrusions, the magma may finally solidify throughout without the formation of visible ore deposits within the upper solidified portion or in cover rocks. Any such disturbance could trigger periods of mineralization; therefore, their timing with respect to the thickness of either the roof rock cover or the solidified upper part of the magma is of greatest importance.

Gray says:

> There are, however, some metals that fit better into the magmatic pattern. Gold veins often, tin, tungsten and beryllium nearly always, occur in or near granite masses. It is obvious that some ore deposits may be magmatic, and a magmatic theory of ore formation can explain and could guide us to them. It cannot, however, explain and would not serve as a guide to the sources of the greater part of our copper, lead, zinc, gold, silver, or uranium production.

From this and other statements appearing in Gray's lecture, the reader must assume that the use of the term "granite" is meant to include the various calc-alkaline rocks, such as grano-diorite, quartz-monzonite, and other types of granitoid rocks. To conform, the present writer also uses the term "granite" in the broader sense.

Thus it appears that Gray rejects all theories of magmatic origin as guides to ore deposits based on his observations that there are no visible granites associated with certain gold and copper deposits in sedimentary rocks, and that only gold veins, tin, tungsten and beryllium occur in or near granite masses. Both Gray and Knight are contending in effect, that because in a few examples granite could not have been used as a guide to the discovery of a number of well known deposits of copper, zinc and lead, we must eliminate not only granites, but quartz-porphyry, granite-porphyry, rhyolite-porphyry, and other intrusive derivatives of granitic magmas, and igneous rocks in general, as field guides to ore deposits.

These facts are well known; (1) that nearly all of the copper produced in the United States, Mexico, Peru, and Chile, is being mined from intrusive porphyries, which, in the present writer's opinion, are genetically related to granites which may or may not be exposed in the mine areas; and (2) many of these porphyry districts also produce large quantities of zinc, lead, and silver, derived from the same magmatic source as the copper. Under such circumstance there seems to be overwhelming support for the theory of magmatic origin as a guide to most of the world's great deposits of our non-ferrous metals. Yet, Gray doubts that the ore metals of a porphyry copper deposit and the porphyry itself are derived from a common magmatic source. He says: "The porphyry coppers are certainly in or near granite porphyry, but there is much more porphyry that is barren, *and little or no evidence in detail to connect the origins of ore and rock.*" (Italics by present writer.) This may come as a mild shock to geologists familiar with porphyry copper ores.

Referring to the Central African copper deposits, Gray states that he abandoned his "original magmatic ideas of their origin when Garlick showed the granites to be older than the cupriferous sediments." He adds that:

> On the Copperbelt the metallic sulphides are concentrated in folds and other structures formed during deformation and in veins which cut and must be later than these structures. Here too, unless we insist upon the former existence of some hypothetical hidden magma, the most probable source of the metals is the sediments themselves.

He concludes therefore, that:

> the evidence indicates that here, as on the Rand, widely dispersed metallic constituents of the original rocks were concentrated during or after folding by the solutions that facilitated the metamorphism.

Thus Gray, agreeing with Garlick (9) and Brummer, denies the existence of a post-Roan age granite. Upon that premise he takes the positive stand that the copper must be of non-magmatic origin, that is, first precipitated from lake or sea water contemporaneously with the materials composing the Roan shale or other sedimentary beds of the Roan series, later to be dissolved by metamorphic water, transported and re-deposited in the Roan shale or wherever now found.

Those of us contending for a magmatic origin for the Copperbelt ores may well raise this question: If either the "syngenetic," or Gray's "metamorphic water" theory has so much merit, why look for a post-Roan granite? Why

did Gray (13) first believe in a magmatic theory of origin after his long and careful day to day mapping study of the Mufulira deposit? What were the facts observed in the mine and drill cores that led him to that opinion? The mere circumstance of the Garlick and Brummer findings that all the known granites in the Copperbelt area are pre-Roan in age, surely did not alter the facts observed by Gray in the Mufulira mine, or by Davidson (5) at Chambishi, or by Jackson (15) at N'changa, or by Bateman (1) in the mine and laboratory, or by Sharpstone in the Roan Antelope! We must assume that it was upon the facts observed at the respective properties that these highly competent and experienced geologists based their conclusions that Copperbelt ores were of magmatic origin. I am certain that the facts of geology and ore occurrences I saw in the Copperbelt mines in 1931 have not altered with time.

While at the N'Kana mine I wrote short summaries of my underground observations on the ore body and on all the diamond drill cores. These may be pertinent here, and I quote:

> Frequently the lower portion of the Roan bed, say 5 to 10 feet of it, immediately above the schist, is only slightly mineralized, running from 0.4 to 2%. Next above comes the main ore width. The better grade ore width has much the appearance of being a mineralized shear zone coincident with the strike and dip of the interior half of the Roan bed. One is immediately struck with the alternate dark and white banding, which is, as it turns out to be, bleached white narrow bands of the shale, alternating with unwhitened bands, plus a lot of later fractures filled with quartz, dolomite and copper sulphides, principally bornite, which coincide in part with the bedding but which cut across the narrow bedding at acute angles. The much lighter aspect of the richer ore therefore is due in part to bleaching of the dark shale beds along bedding planes or cross-fractures. On the whole one cannot get away from the conclusion that there has been some strike fracturing in and along the Roan shale subsequent to the general regional folding, and that this fracturing was in fact the channelway along which the uprising ore solutions came. I saw numerous examples of these late quartz and bornite fractures cutting right across the layers and across drag folds.

And in summarizing my observations on drill cores examined, I wrote:

> From this drill hole information, one and only one conclusion is acceptable, which is, that the copper, quartz and cobalt minerals were brought in by solutions originating somewhere down the dip of the beds, that they followed avenues most permeable to travel, and from these solutions the minerals were deposited in cracks and fissures and bedding planes which provided the channelways, and in disseminations throughout the body of the rock, in part at least through process of diffusion, but limited to inches or feet outward from the channelway.

The 1929 geological map of the N'Kana Concession shows a considerable amount of gabbro intruding Roan sediments in the N'Kana-Chambishi area. According to Garlick's map a thick gabbro dike intrudes Roan rocks just beneath the Chambishi ore body. Possibly more significant are both the granite dike intruding the lower Roan beds at N'Kana No. 1 shaft, and a 50-foot gabbro dike cutting through the Roan shale ore bed[1] on the N'Kana 1,630 foot level. At this intersection a zone of shear planes within the shale

[1] V. D. Perry, personal communication.

bed cuts through the dike. It is continuously mineralized with stringers of glassy quartz containing bornite, the copper-iron-sulfide mineral characteristic of Copperbelt ore throughout the area. There can be no question that the dike is post-Roan and post-folding in age, and that the fissure zone and the ore minerals are post-gabbro.

Davis (6), whose studies were confined to the Roan Antelope mine, says the Muliashi gabbro has never been "seriously advocated as a source of the ore." Why not, in view of the difficulties he had trying to establish a syngenetic origin for his hypogene sulfides, bornite and chalcocite? A deeper mass of gabbro could well be Gray's hypothetical hidden magma responsible for the source of the metals. In view of this possibility it may be of some significance to call attention to the fact that elsewhere in Africa there also appears to be a widespread association of copper deposits with gabbro. A body of intrusive gabbro showing much disseminated chalcopyrite occurs near the rich Kipushi copper ore body, and in southwest Africa the important O'okiep ore bodies are mineralized diorite and gabbro.

But before ruling out the existence of a post-Roan granite in the Copperbelt area, a further study seems highly desirable in view of the exposure of a granite dike intruding lower Roan sediments in N'Kana No. 1 shaft, and the reported occurrence of post-Roan pegmatite dikes in the N'Changa mine area.

To date it does not appear that Gray, Davis, or Garlick, while denying the possibility of magmatic source for the Copperbelt ore solutions, have taken into consideration the many different types of ore deposits occurring in the area. Knight and Sullivan apparently accept as proved, a syngenetic origin for these Northern Rhodesian deposits, with the implication that the ores are confined strictly to the Roan shale bed, neither of which is a fact. At Baluba near the Roan Antelope mine the chalcopyrite-linnaeite mineralization is in the schist band immediately below the shale bed. At Chambishi in one area a large high grade (5 to 8% Cu) chalcopyrite-bornite ore body replaces the schist band beneath the shale. The lower part of the shale in contact with the high-grade ore contains enough finely disseminated bornite to constitute ore grade. The upper shale ore limit, a very irregular one, is determinable only by assay. In the easternmost part of the Roan Antelope syncline the minable ore width includes the schist band and the lower two-thirds of the shale bed. In one deep N'Kana mine drill hole only the schist band beneath the shale bed is mineralized. At Mufulira the principal ore beds are mineralized quartzite, not shale. The N'Kana and Mufulira ore bodies are well defined "ore shoots" of limited lateral extent, pitching steeply down the dip of the beds. In the N'Changa the copper minerals are in the Roan shale, in quartzites above and below the shale bed, in arkose below the lower quartzite, and also as replacements in limestone above the upper quartzite. In one N'Changa drill hole the Roan shale bed is said to be barren although the quartzites above and below it are heavily mineralized with copper sulfides. Assuming that all the copper of the Copperbelt ore deposits was originally syngenetic with the Roan shale, the explanation of the gymnastics of redistribution of the copper

to form the ore bodies and their variations above described is a problem, the solution of which may well be left to the syngeneticists.

However, bearing directly upon this problem of copper transport we learn from Davis, who, after careful laboratory study of Roan Antelope ores states:

> It is concluded that mineralization is of pre-folding age, and that the sulfides recrystallized during metamorphism together with other rock constituents. In the general case this occurred in situ and relatively late, so that sulfide grains became most irregular in shape as they found place for themselves among the silicates by fitting between or molding around them or replacing them. In places of high stress, sulfides also migrated during metamorphism to replace and cut across silicates in veinlets, stringers, along cleavage and other places of tensional relief.

This means that Davis found evidence of but little movement of the "syngenetic" copper of the shale during active metamorphic processes accompanying folding. Obviously, the concept of only a small movement of the copper from where it was deposited in the lagoon mud fails utterly to account for the wide distribution of copper in the many different types of ore occurrences throughout the Copperbelt previously noted.

Gray believes, apparently, that the conclusion offered by Davis is in error, because he says, "I believe the evidence indicates that it is the 'metamorphic' water that transports and concentrates widely dispersed metals contained in the sediments." The only sediments in the Copperbelt area from which metamorphic water might have been squeezed were those of the Roan Series, including the Roan shale, resting upon eroded pre-Roan granites and schists. The "widely dispersed metals" must have been syngenetic with the sedimentary beds according to Gray's theory.

In the Copperbelt, Garlick maps gabbro intruding the Roan Series in the Muliashi area just west of the Roan Antelope mine and, according to G. R. Davis, it is toward this area that tourmaline becomes more abundant. Davis also notes that elements other than copper, such as arsenic, antimony, nickel, cobalt, selenium, and tellurium, although present only in small quantities in the Roan Antelope mine, become increasingly abundant toward the Muliashi area. "More important," Davis goes on to say, "sulfide zoning points to a source in this direction." Although not mentioned by Gray this copper-iron-sulfide distribution pattern bears directly upon the problem of the origin of the Northern Rhodesian copper deposits.

The remarkably fine example of mineral zoning described by Davis extends from the Roan Extension to the most easterly outcrop of the Roan shale, a distance of five miles or more. The zoning is from chalcopyrite-pyrite in the Roan Extension, successively through chalcopyrite-bornite, bornite-chalcocite, to chalcocite in the most easterly portion of the syncline. The change from one copper sulfide to another is a gradual one always overlapping, never sharp, and, significantly, conformable with the strike of the axis and form of the synclinal trough.

The zoning of the copper minerals which represents an increasing sulfur to copper ratio toward the west, together with the increases in the quantities of tourmaline and the rarer elements in that direction, suggests that the source

of the copper-bearing ore solutions was deep in the Muliashi basin to the west of the Roan Antelope mine, and that the copper minerals were added to the shales of the Roan syncline after folding and metamorphism. It is extremely unlikely that pre-folding distribution of pyrite and the copper minerals in the lagoon mud, even under varying shore line conditions, or with bacterial aid, could have been such as to conform so perfectly with the mineral zoning exhibited throughout the synclinal fold, or that the direction of the axis of the folding could have been influenced by pre-folding distribution of the copper, iron, and sulfur, in the lagoon mud! Nor can the present writer visualize Gray's "metamorphic waters" collecting "widely dispersed" copper from Roan sediments of the vicinity and transporting it to form a centralized ore solution source deep in the Muliashi basin just to the west of Roan Extension.

The admissions of Davis on the subject of zoning of the copper-iron-sulfides are so pertinent to the question of origin that they must be noted here, and I quote from his article as follows:

> There are indications of various kinds that the shales were deposited in a water body neither very deep nor of appreciably variable depth. A theory of detrital deposition of the sulfides is untenable for numerous reasons. Copper and iron carbonates precipitated inorganically from sulfate solutions in an alkaline environment might be converted during early diagenesis to sulfides by hydrogen sulfide liberated from organic matter. An inorganic process such as this, in common with a detrital theory, cannot account for either the zoned arrangement of sulfides or the sharp cutoff to mineralization at the hangingwall in homogenous rock.

With that statement the present writer is in full agreement. However, Davis then goes on to say, "There remains a bacterial origin for the sulfides," and he adds that Garlick "has worked out a mechanism to account for both syngenetic sulfide deposition and sulfide zoning on the Copperbelt" through "precipitation from stagnant waters by anaerobic bacteria in the presence of organic matter, and claims successful predictive use of the theory." The theory of Davis and Garlick demands that the copper sulfide zoning, caused by bacteria, took place in the Roan lagoon mud before any folding or metamorphism of the Roan series. This is in complete disagreement with Gray's "metamorphic water" theory, and it is in my opinion, a wholly inadequate and unacceptable explanation.

From facts brought out through the careful laboratory studies of the copper-iron-sulfur relationships by Bateman and Davis, the only sound conclusion possible is that the orderly five-mile zonal arrangement of copper sulfides in the Roan Antelope syncline took place after the folding and metamorphism of the Roan shale. Furthermore, comparing it with copper sulfide zoning at Butte, Montana; Cananea, Mexico; and in other districts with which this writer is familiar, the copper-iron-sulfide mineral zoning in the Roan Antelope may be explained very satisfactorily under the theory of sulfide deposition from hydrothermal solutions derived from an igneous source. The west to east zoning at Roan Antelope was controlled by varying quantitative ratios between the sulfur, copper, and iron, present in solution. The

changing ratios could have been brought about by decrease in temperature, pressure, and by selective deposition, aided by diffusion gradients possibly consequent from chemical attack on some of the constituents of the rock through which the solution traveled upward from its source.

Bearing directly upon the question of origin of Copperbelt ores will be future determination of the zonal behavior in depth of the copper minerals of the N'Kana and Mufulira ore shoots. If deep mine developments should show a downward mineral zoning change to a chalcopyrite-pyrite combination as exhibited in the Roan Antelope ore body toward the deep source in Muliashi basin, the proponents of a magmatic solution origin for Copperbelt ores will have an additional strong argument, in the opinion of this writer.

In more recent studies on Copperbelt sulfide ores, Bateman and Jensen (4) have determined that, in part at least, the mineral "chalcocite" of previous papers is digenite. And as to ore genesis, summaries of evidence presented by the authors seem to pose much greater problems for the syngeneticists than for the proponents of the magmatic theory, in the present writer's opinion.

To return to the discussion of the theory favoring "metamorphic waters" as agents of ore formation in general, Gray states that mountain ranges are "great masses of sedimentary rocks, shales, sandstones and limestones, that could have been formed only in water, mostly in the sea; and of metamorphic rocks derived from them. There they are for all to see, folded, broken and squeezed sometimes almost beyond recognition into what we call schists and gneisses." The logical inference to be drawn from that statement is that water and significant amounts of metals are present in nearly all, if not all, sedimentary rocks prior to the time of folding. In other words, the metals of ore deposits are syngenetic with the sediments.

Conclusions of great economic significance could be drawn from such a line of reasoning. But, in the United States as elsewhere we have range after range made up of great thicknesses of folded, faulted, and squeezed sedimentary rocks of all ages. It so happens, unfortunately, that they contain important ore bodies of the type under discussion here only where invaded by igneous rocks. Prior to igneous intrusions, the mountain building processes should have squeezed out a large amount of metamorphic water which, under the Gray hypothesis should be suitable for transporting metals, but no ore deposits were formed. One must conclude that the absence of ore deposits not associated with igneous rocks is because; (1) the rocks forming the mountains contained too little of the metals; or (2) the circulating metamorphic waters were present in insufficient quantity to provide metal transport; or (3) the water present was incapable chemically of dissolving the metals. Actually, under the metamorphic water theory, prospecting the highly folded and metamorphosed sedimentary and basement rocks of the Swiss Alps should be an attractive venture. This great mountain area appears to have everything needed under such a theory, but it contains no ore deposits of importance.

On the problem of re-deposition, I can agree with the syngeneticists when they state that the re-deposition of the metals is one of their great problems.

But no less so, in my opinion, than that of establishing their source, getting them into the lagoon muds, and finally, that of re-solution and transport to where we now find them. I have no hesitancy in saying that in the above respects the problems of distribution and deposition are much greater for the syngeneticist than for the proponents of the theory of magmatic origin.

The theory of magmatic origin for ores involves high-temperature solutions originating at a deeper source that may be completely foreign to the rocks in which the metals are deposited. From that deeper source the solution with its load of metals and sulfur moved upward into an entirely different environment, meeting declining temperatures and pressures, and coming into contact with rocks that may be of a widely different chemical composition from that from which the metals and solutions were derived. With changing wall rocks, chemical reactions are set up which alter the composition of the solution and seriously affect the solubilities of some or all of the metals carried in solution. No doubt, these changes are important contributing causes to mineral deposition and to mineral zoning. Merely because of the fact that an igneous source rock is not visible in the immediate vicinity of an ore body in a sedimentary formation, the adoption of a theory of syngenetic or metamorphic water origin can not be justified.

The ultimate "clinching" stock argument of those favoring the "syngenetic," or the "metamorphic water," origin of ore deposits in sedimentary formations, is the absence of visible granite within the immediate vicinity of the deposit. This out-of-sight source of ore-bearing solutions is not more applicable as an argument against a magmatic ore solution than it is one against a non-magmatic source. In this respect each ore deposit is its own problem, and the theory of origin most acceptable would be the one based on all of the available facts of geology surrounding the deposit. Easy to say, of course, but often it is the different interpretations of meaning assigned to the observed facts that starts the argument. The condition, a very common one, however, that the actual source-point of the ore solutions and metals is out of sight, is a weak argument for either side. But it may serve as the final escape clause for those who prefer to speak in general terms.

The present writer realizes that the actual source point of a "magmatic" ore solution is one of the least understood problems of ore genesis, even where the deposit is believed to be genetically related to an igneous rock, as at Butte for example. But by comparison, as to being "out of sight," nothing could be farther out of sight than the immediate or ultimate source of the placer gold of the Rand, or the "syngenetic" copper of the Copperbelt deposits. No proponent of a syngenetic or metamorphic water origin appears willing to come forward with an answer, except one couched in generalized terms. They have no other choice. Scores of geologists arguing for years for a syngenetic origin of the copper sulfides of the "classic" Mansfeld ore deposit, never could agree upon where the copper came from. If that isn't an "out-of-sight" source, what is it?

We must now examine the implications of the theories as they bear upon the future of mineral exploration. The genesis of ore deposits have been

the subject of study by geologists for more than a century. Various theories of origin have been advanced with volumes written in their support, or in opposition. Near the end of the nineteenth century came the realization that a better understanding of the genesis of ore deposits could be made helpful in the search for ore. The idea, born of the geologist in mine and field, resulted in intensive mapping and study of ore occurrences. Soon research on the origin of ores was in order in laboratories of governments, universities, and mining companies. Significantly, much research work in the past and up to the present, has been directed toward the problem of how ore fluids are derived from crystallizing magmas. This line of investigation was, and is, based upon the almost universal recognition of the fact among geologists that most of the world's important ore deposits are genetically related to magmas. Recently Bateman (3) wrote: "Magmas are the source of essentially all of the important mineral deposits."

However, Gray concludes that *"if more mining geologists will relax their obsession with the theoretical possibilities of hypothetical magmas, and help to solve the structural and chemical problems of metamorphism, we may have in the near future the understanding needed to guide us to ore deposits."* (Italics are present writer's.)

That statement is a short summary of unsound advice to mining and field geologists everywhere. There is implied also an unwarranted criticism directed toward those who, through wide experience in the field, have been compelled to recognize and accept the vitally important part played by granite and its derivatives, and other igneous rocks, in the genesis of ore deposits. Furthermore, Gray in effect, is suggesting that we discard the teachings and findings of many of the world's best known students of ore deposits, such as Lindgren, Vogt, Kemp, De Launay, Spurr, Graton, Bateman, W. H. Emmons, and a host of others.

The present writer's reply to Gray and to Knight is that if exploration geologists, now or in the future, go into the field looking for ore deposits while holding a deep prejudice against granite and other igneous rocks as sources of ore, the "science of ore finding," if I may call it that, and the rate of discovery of new ore, will receive severe setbacks. The suggested study of the "structural and chemical problems of metamorphism," however laudable under certain circumstances, can never eliminate or lessen the important part played by igneous activity in the genesis of ore deposits.

THE ANACONDA COMPANY,
BUTTE, MONTANA,
Dec. 4, 1959

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APPLICATION OF THE SPHALERITE GEOTHERMOMETER TO SOME NORTHERN NEW BRUNSWICK SULFIDE DEPOSITS

DAVID BENSON

ABSTRACT

The base metal sulfide deposits of northern New Brunswick were studied with special emphasis on temperature determinations made with the sphalerite geothermometer.

The iron content of the sphalerite was determined by x-ray fluorescence analysis of 0.25 mg samples drilled from the surface of the polished sections. Appreciable differences in the iron content of adjacent areas of sphalerite are attributed to varying amounts of iron picked up by the sphalerite from the replaced minerals. Exsolution pyrrhotite was found to be the only reliable evidence that sphalerite formed in the presence of excess iron.

The temperature of formation of the Heath Steele and Brunswick mines is given as 610° C at 2,000 bars, equivalent to burial under 15,000 feet of younger rocks.

INTRODUCTION

THE sphalerite geothermometer, as developed by Kullerud (*7*), has been accepted as a valid concept. The method, which is dependent on the composition of FeS–ZnS mix crystals, has been applied to more than 100 sulfide bodies.

It was thought that a study of the mineralography of the sulfide deposits of northern New Brunswick coupled with temperature determinations made through use of the sphalerite geothermometer, would be a useful evaluation of Kullerud's method. The writer believes that the sphalerite geothermometer must be used with more caution than has been used previously.

The sulfide deposits are found in an interbedded sequence of sedimentary and volcanic rocks of Ordovician age that are intruded by Devonian granites and gabbros.

Acknowledgments.—Dr. G. R. Webber of McGill University directed the research and has shown particular interest in all phases of the work.

I would also like to thank the various company geologists who aided in collecting the suite of samples.

PREVIOUS WORK

The most recent work of the sphalerite geothermometer was published by Barton and Kullerud (*3*) in 1958. They give a new diagram relating the iron content of sphalerites to the temperature of deposition. They conclude that sphalerite formed in equilibrium with pyrrhotite at temperatures below 500° to 600° C can be used as a geological thermometer. However, it is not

possible to determine the temperature of deposition before the sphalerite has been analyzed for iron content in order to use Kullerud's curve. The limiting factor in choosing sphalerite to be used for temperature determinations is therefore its environment of formation.

Several authors have used the presence of pyrrhotite in association with sphalerite as indicative that the sphalerite was formed in equilibrium with the pyrrhotite. They do not state any lower limit as to the amount of pyrrhotite that must be present.

It is of special interest to note the method of sample preparation and analysis used by previous workers. Kullerud and Newman (8) obtained a pure sample by grinding the sulfides to 70 mesh, then hand picking the sphalerite fraction from a heavy liquid concentration. Analysis was by wet chemical and x-ray diffraction methods. Kullerud, Padget and Vokes (9) obtained samples for analysis through use of a Frantz Isodynamic Separator, heavy liquids and hand picking under a binocular microscope. Samples from the Star Mine were prepared by crushing several times and final hand picking of the coarse grained massive sphalerite (6). Lovering (10) does not give his method of sample preparation so it is not known whether he was aware of the depositional environment of his samples. Skinner (12) has stated: "Polished sections show the sphalerite to be quite clean and not to contain exsolved pyrrhotite or chalcopyrite. Two sphalerites have been separated and analyzed." It is probable that the sphalerite samples represent non-equilibrium conditions of formation. Sphalerite samples of from 15 to 40 mg were drilled from the surface of polished sections by Assad (2). The size of the samples suggests that grains with different iron content were often used in a single sample.

It is suggested that pyrrhotite found in association with the sphalerite is sufficient proof that the sphalerite was formed in the presence of excess iron. However it is not known how close this association must be. The method of sample preparation used by previous workers is such that they can never know what minerals were in contact with their sample grains. Thus they have assumed that the presence of pyrrhotite somewhere in the sulfide deposit is proof that every grain of sphalerite formed in an environment containing excess iron.

The author believes that a closer scrutiny of the sample area and a thorough knowledge of its depositional environment is necessary before sphalerite can be used as a geological thermometer.

ANALYTICAL PROCEDURE

About 300 polished sections were carefully studied to find 74 areas of sphalerite that could be sampled. These sample areas were examined with an oil immersion lens and the areas that contained impurities were discarded. A sample weighing about 0.25 mg was drilled from the surface of the polished sections. The drilled area was re-examined and the sample was discarded if any impurities were noticed at the bottom of the drilled area. The ZnS/FeS concentration ratio in these samples was determined by x-ray fluorescence

spectrography, using an adaption of a method developed by Chodos, Rose and Godijn (4). The sample holders were made by stretching a thin (0.00025") film of "Mylar" (DuPont of Canada, Ltd.) across a frame of Lucite. The sample rested on the "Mylar" film in a small dimple centered in the middle of the brown out pattern.

The relative deviation was tested by using four standard sphalerite samples provided by Chodos (4). The standard deviation for a sphalerite sample containing 12.29 weight percent FeS was 0.27, equivalent to 10° C, or 2.19 percent when expressed as a relative deviation.

RESULTS OF ANALYSES

The temperatures have been calculated for normal pressure for it is not certain what portion of the younger sediments were overlying the region at the time of formation of the sulfide bodies. As estimated from Week's (13) description of Appalachian geology, the mineralized area may have been covered by from 7,000 to 20,000 feet of younger formations at the time of the mid-Devonian intrusions, when the sulfide bodies attained their present form. This would correspond to confining pressures of 1,000 to 3,000 bars, which are equal to a rise in the temperature of formation of 25° to 75° C. The author has assumed the overlying section to have been about 15,000 feet which would mean an additional 50° C should be added to each determination.

The pressure differential between samples would be only 0.34° C for each 100 feet of depth. This value is smaller than the limit of error for the method of analysis used, so is not taken into account.

The temperatures obtained for individual samples from the Brunswick No. 12 mine are shown in Figures 1 and 2. The average value for sections that had visible pyrrhotite is 450° C and the value is 420° C for sections without visible pyrrhotite. It was not possible to disprove the presence of pyrrhotite in any sections as exsolution blebs less than 1 micron large have been found in many sphalerite grains, and smaller blebs, not visible under the microscope are likely. The proposed temperature of formation is about 555° C, the value obtained from sample No. 84 which probably formed in the presence of excess iron.

Temperatures determined for the Heath Steele "A" open pit are shown in Figures 3 and 4. The temperature of formation for this sulfide body is given as 560° C from sample No. 1 which contained considerable exsolution pyrrhotite. The average value for sections with visible pyrrhotite is 480° C whereas those without visible pyrrhotite have an average value of 425° C.

DISCUSSION

The writer had hoped to examine the evidence of temperature zoning in the sulfide bodies under investigation. Although all the sections examined contain sphalerite, many of them do not contain sufficient pyrrhotite to indicate the presence of excess iron at the time of deposition. The inability to find pure sphalerite grains also contributed to only 68 out of 217 sections

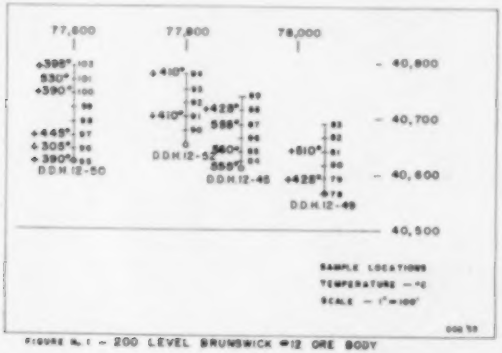

FIGURE 1 — 200 LEVEL BRUNSWICK #12 ORE BODY

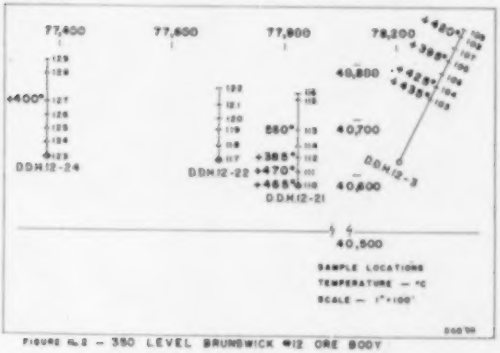

FIGURE 2 — 350 LEVEL BRUNSWICK #12 ORE BODY

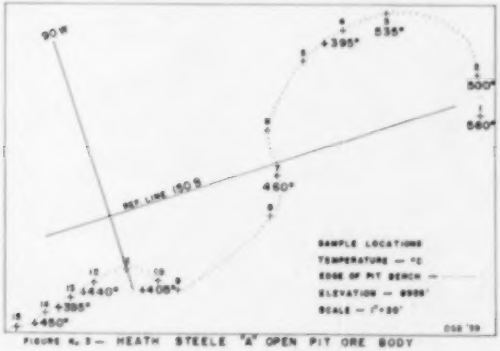

FIGURE 3 — HEATH STEELE "A" OPEN PIT ORE BODY

yielding samples that could be analyzed. Two samples were obtained from each of 6 sections.

The temperatures are broken down into those from sections where pyrrhotite was positively identified and those in which no pyrrhotite was identified.

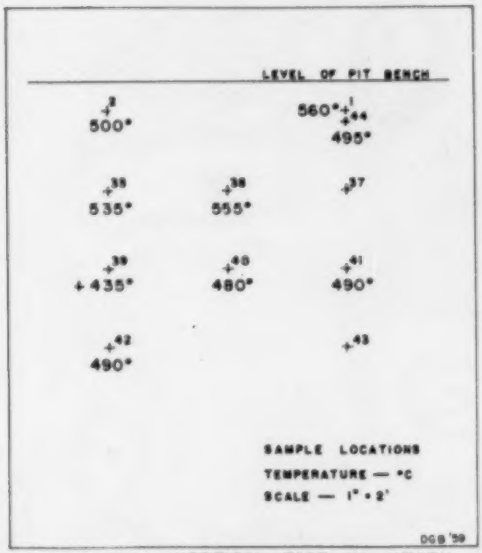

FIGURE No. 4 — VERTICAL FACE IN HEATH STEELE "A" ORE BODY

The average temperature for all sections in the former category is 455° C and for the latter group it is 400° C. Temperatures considerably higher or lower than the average value are found within each group.

The variation in results from the sections not containing pyrrhotite is explained by examination of Barton and Kullerud's graph. At a temperature of deposition around 500° C, sphalerite in such an environment may have between 5 and 15 weight per cent FeS in the crystal lattice. Formerly, sphalerite was thought to be in equilibrium with excess iron at the time of formation if it was found to co-exist with pyrrhotite. This does not seem to be true. At first glance it would appear that each polished section is an isolated system unto itself. Thus the conditions of deposition would apply only to a very limited volume. Examples of such results are found in the following instances: 1) 2 samples (No. 1 and 44) from the vertical face in Heath Steele "A" ore body differ in temperature by 65° C though only 6 inches apart; 2) on the 200 level of Brunswick No. 12 there are 3 samples (No. 100, 101 and 102) that vary from 390° to 530° to 395° C within 50 feet; 3) at the same location as the preceding case there are 2 samples (No. 87 and 88) 25 feet apart that differ 130° C from each other. These variations are found because the sphalerite with the lower iron content was not formed under equilibrium conditions with excess iron. Mineralographic study has disclosed only one period of sphalerite, thus the variations cannot be explained

by different periods of mineralization each with its own temperature of deposition.

Further work was done on this problem with 6 sections from which it was possible to get 2 separate samples. These pairs of samples may both be from identical environments, from similar environments or from totally different surroundings within a single section. The results are best discussed singly.

Section 41 is from the "A" ore body of Heath Steele Mines. It is a poor polished section with a few large cavities making up much of the surface area. The remaining area is 60 percent pyrite, 15 percent sphalerite and 2 percent chalcopyrite. Both samples are from the same environment but one includes a grain with exsolution pyrrhotite while the other does not have any pyrrhotite. The samples are from areas 6 mm apart and give temperatures of 490° and 310° C for the grains with and without exsolution pyrrhotite respectively. Obviously, the temperatures at time of deposition did not vary this much, and the answer must lie in different conditions of formation.

Section 42 although from the same ore body as 41 differs slightly in mineral content. The approximate composition is 50 percent pyrite, 40 percent sphalerite and 10 percent galena. The samples are taken 9 mm apart from a band of sphalerite, 13 mm wide, within a more massive pyrite section. A low temperature of 430° C was obtained for one sample while the other which had minor exsolution pyrrhotite gave a value 60° C higher. Again the depositional environment seems to be the answer.

No pyrrhotite was observed in Section 81 from Brunswick No. 12 ore body. The sulfides present were sphalerite 50 percent, pyrite 5 percent and galena 3 percent. Temperatures of 420° and 510° C are given for the two samples which are from areas about 9 mm apart. None of the sphalerite seems to have been formed in the presence of excess iron but the iron content is almost as high as in sphalerite co-existing with pyrrhotite.

Section 91, also from Brunswick No. 12 ore body, contained about 70 percent pyrite, 10 percent sphalerite, 1 percent chalcopyrite and 2 percent galena. Two very small samples were removed from areas about 2 mm apart. The temperature values are 340° and 410° C but should not be strongly stressed due to the small samples. They do however fall into the general pattern.

Two narrow (2 mm) bands rich in sphalerite and about 15 mm apart were sampled from Section 104 from Brunswick No. 12 ore body. These samples were run by the same method but on two separate days and gave results of 420° and 425° C. The polished section was 50 percent pyrite, 40 percent sphalerite and 5 percent galena and no pyrrhotite was seen.

The most interesting results were from polished Section 110 from the Brunswick No. 12 ore body. This section consisted of 35 percent carbonate gangue, 50 percent pyrite, 10 percent sphalerite and 2 percent galena. One sample, taken from sphalerite in a matrix of carbonate gave a temperature of 335° C. The other sample found in a pyrite matrix 6 mm away gave a value of 465° C. The iron content of the sphalerite is probably due partly to the iron content of the replaced mineral. In this section little or no iron was

found in the carbonate so the iron content of that sphalerite must have come from the transporting medium. The extra iron in the other sample was probably due to minor replacement of the pyrite matrix.

From these examples it appears that the environmental conditions at the time of deposition must be worked out for each individual sample area. Microscope work with the polished sections showed that individual sphalerite grains could vary in composition from each other. There are several places where a single sphalerite grain has a few exsolution blebs of pyrrhotite, but an adjacent grain is barren. Kullerud (7) states that the presence of manganese and or cadmium in the sphalerite lattice may inhibit the exsolution of pyrrhotite. It was not possible to sample and analyze individual sphalerite grains. Thus the observation that individual neighbouring sphalerite grains formed at the same time may have slightly different compositions has not been proved by analyses.

The presence of exsolution pyrrhotite in a grain of sphalerite indicates that the grain of sphalerite was in equilibrium with iron either at the time of formation or during the period of cooling. A careful search was made for sphalerite that had considerable exsolution pyrrhotite evenly distributed over an area large enough to be sampled. It was assumed that such a concentration of pyrrhotite is indicative of excess iron being present at the temperature of formation, or soon after the cooling began. These grains of sphalerite plus the exsolved pyrrhotite were analyzed and the total iron content was used to determine the temperature of formation. The author does not believe that the temperatures obtained from these grains can be used as an exact temperature of formation. They indicate only the temperature of the sphalerite when the pyrrhotite began to exsolve, but this temperature is thought to be close to the temperature of formation of the sphalerite.

Thus the presence of pyrrhotite in close association with sphalerite does not indicate that the needed excess iron was found in the system at the time the sphalerite was formed. Exsolution pyrrhotite is not proof either, but only suggests the existence of more iron than is otherwise found. The analyses suggest that some of the iron, perhaps a minimum of about 8 percent, was present in the complex ion in which form the sphalerite was transported. The remaining iron is due to variations in this minimum amount and to the iron content of the replaced grains. The iron content of the replaced grains is distributed throughout the actual replacing grain and not into any neighbouring grains.

Only one third of the samples from the edge of the open pit bench in the Heath Steele "A" ore body show possible equilibrium conditions of deposition. Two of the remaining samples are from sections that contain pyrrhotite, while no pyrrhotite was identified in the remaining 4 samples. The temperature of these 6 samples is similar, suggesting that all the sphalerite was formed under the same conditions. Only Section No. 1 had evenly distributed exsolution pyrrhotite throughout the sample area. Other sections have minor exsolution pyrrhotite but it is restricted to single grains of sphalerite. Nine polished sections were collected on 2-foot centres from a vertical face below

Sections No. 1 and No. 2. Six of the eight samples analyzed are from sections that have visible pyrrhotite. None, however, possess sufficient pyrrhotite to indicate a temperature of formation. This part of the ore body is said to have been deposited at 560° C, the value obtained from Section No. 1.

Arnold (1) gives the same temperature of formation of 550° C at 2,000 bars, for sphalerite co-existing with pyrrhotite and pyrite, and for pyrrhotite, from a sample from Heath Steele Mine. The pyrrhotite temperature is given at 1,000 and 2,000 bars and the sphalerite temperature at 2,000 bars for he is apparently uncertain as to the thickness of the overlying cover at the time of deposition. The average sphalerite temperature obtained from all sections that contain pyrrhotite is 490° C at normal pressure or 540° C at 2,000 bars. These values must be considered as the temperature of the sulfides at some time after their formation, perhaps shortly after they began to cool. The value from Section No. 1 when corrected to 2,000 bars gives a temperature of 610° C, which is about 50° higher than that proposed by Arnold.

One sample from Brunswick No. 12 contained minor amounts of what appeared to be pyrrhotite. The mineral was visible only with an oil immersion lens so that positive identification was not possible. The value of 555° C obtained from Section No. 84 is proposed as the temperature of formation for this ore body. No exsolution pyrrhotite was found in any of four other samples that gave temperatures from 530° to 560° C. These may also represent the true temperatures of formation. Scrutiny of the other values reveal that non-equilibrium conditions existed irregardless of the co-existing minerals.

The New Brunswick sulfide bodies are characterized by extremely fine grained mineralography. This made it difficult to find large enough areas to sample, and to find areas composed of grains that had identical compositions. The only indication of variation in iron content is the visible exsolution pyrrhotite. This proved to be different for many adjacent grains so that it is probable that most of the sphalerite varied from grain to grain. Rose (11) has found that a single sphalerite crystal, of unstated size, varies in iron content from one end to the other. With sulfides of coarser grain the sampling procedure would be simplified. If sphalerite with known excess iron could be removed in sufficient quantities for analysis from a suite of samples, a study of temperature zoning could be made. However the difficulty of knowing whether sufficient iron was present at the time of formation cannot be overcome. Samples with exsolution pyrrhotite must be chosen or minimum temperatures will be the result.

CONCLUSIONS

A suitable method of x-ray fluorescence analysis of 0.25 mg samples of sphalerite was developed. The results compare favorably with conventional analysis of larger samples. The temperature of formation of the Heath Steele and Brunswick mines is given as approximately 555° C at normal pressure or 605° C assuming confining pressure of 2,000 bars.

The results of the analyses and examination of polished sections showed that adjacent areas of sphalerite may have different iron content. The writer believes this variation in composition to be due largely to the amount of iron in the mineral that the sphalerite replaces. Temperatures of formation obtained from sphalerite-pyrrhotite or sphalerite-pyrrhotite-pyrite assemblages must be used with caution. Only those grains that show irrefutable evidence of co-existence with excess iron may be used for true temperatures of formation. All other samples will give minimum results.

47 Ballantyne North,
Montreal West, Quebec, Canada

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STRUCTURE AND STRATIGRAPHY OF THE MANGANESE DEPOSITS OF VISAKHAPATNAM AND SRIKAKULAM DISTRICTS, INDIA

J. S. R. KRISHNA RAO

ABSTRACT

Studies of the manganese deposits of Visakhapatnam and Srikakulam districts indicate that they were originally sedimentary, that they form part of the khondalite series of Eastern Ghats and were subjected to severe structural deformation as were the enclosing formations.

INTRODUCTION

FERMOR (2) considered that the manganese ores of Visakhapatnam were related to "kodurites," a series of igneous rocks ranging from ultrabasic to basic, intermediate, and acid varieties constituting a petrographic province. The validity of "kodurites" being igneous intrusives was questioned and criticised by Cross (1) who suggested a hybrid origin due to assimilation of manganiferous sediment by granite. Although this suggestion was accepted as plausible by Middlemiss (6), then the Director of the Geological Survey of India, no attempt was made subsequently to revise the original ideas of Fermor on these deposits, and the erroneous beliefs continued in many text books on ore deposits.

The author has been interested in these deposits for a long time and carried out detailed geological mapping under the guidance of Professor C. Mahadevan, Andhra University, Waltair, India. The results are presented in this paper. The work was carried out as a Government of India Scholar (1953–55) and as Research Fellow of the National Institute of Sciences of India (1955–57) and I am thankful to both organisations for the financial aid. I am also thankful to the many Visakhapatnam mining companies, and particularly to "Seth Durga Prasad Mining Co.," Koduru. My sincere thanks are due to Prof. C. Mahadevan for his keen interest and encouragement during the progress of the work.

It may be noted that former Vizagapatnam or Visakhapatnam was recently split up into two districts, namely Visakhapatnam and Srikakulam for administration purposes. Most of the type deposits discussed here fall under the zone of Srikakulam District.

LOCATION OF THE DEPOSITS AND ACCESSIBILITY

The area under study is a part of Visakhapatnam and Srikakulam District of Andhra Pradesh, South India. The general location of the area is shown in Figure 1 and that of the manganese deposits in Figure 2. The

table given below shows the location of the type deposits where detailed field and laboratory study was carried out.

Locality	Longitude	Latitude
Koduru area	83° 31 83 34	18 15 18 17 30
Garbham area	83 25 83 29	18 21 18 23 30
Aitemvalasa area	83 34 83 36	18 21 18 23

The Koduru and Garbham group of mines lie three and twelve miles respectively from the Garividi railway station, which is situated 57 miles north of the Waltair-Calcutta main line. Motor roads connect the mines to the railway station. Chipurupalle is the nearest railway station to the Aitemvalasa area, which is three miles further north of Garividi village.

GEOLOGICAL FORMATIONS

The following is the general sequence of strata in the manganiferous areas of the district.

Recent — Laterite and alluvium

Igneous — Pegmatites, granite gneisses

Interaction Rock Types "Kodurites"

Para-gneisses, Khondalites:
- Quartzites
- Garnetiferous quartzites
- Quartz-garnet—sillimanite-graphite gneisses
- Calc-granulites
- Manganese silicates
- Manganese ores (primary)

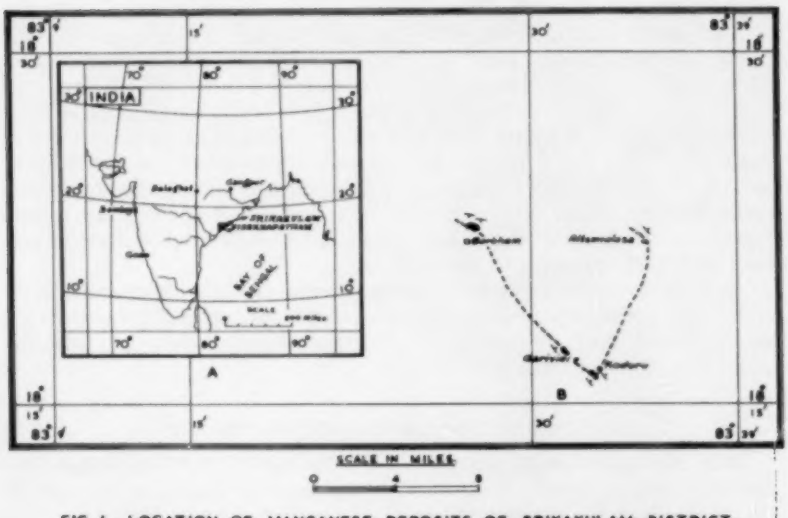

FIG. 1. LOCATION OF MANGANESE DEPOSITS OF SRIKAKULAM DISTRICT.

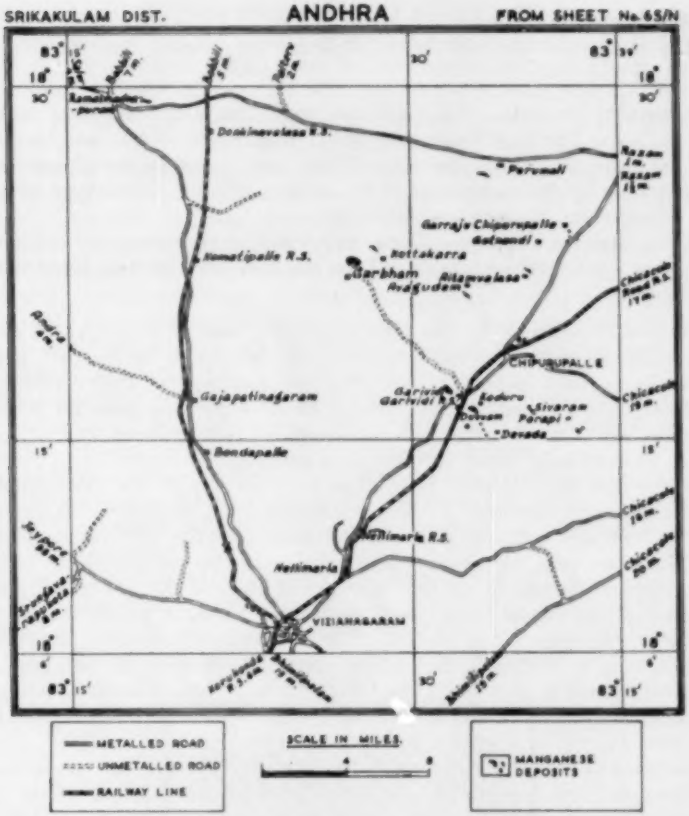

FIG. 2. Location of manganese deposits.

The geological formations consist mainly of Khondalites, (7) namely quartz-garnet-sillimanite-graphite gneisses, quartzites and calc-granulites. The manganiferous rocks consisting mainly of manganese silicates such as spessartites, spandite and rhodonite; the primary bedded ores are also included and considered as a part of the khondalites in view of their close association and conformable nature with other para-gneisses in the field. These para-gneisses, representing original argillaceous, arenaceous, calcareous, and manganiferous members of the eastern ghat rock suites, are intruded by granites and pegmatites, which in places assimilated a part of the country rock. Where an ore body was assimilated it resulted in the formation of the interaction rock types rich in manganese.

STRUCTURE OF THE MANGANESE DEPOSITS

The manganese deposits in the area can be grouped into the following three types:

1. Bedded Deposits.—These are syngenetic and laid down along with the para-gneisses: The type localities being in Koduru, Garbham, and Garividi.

2. Massive Botryoidal Deposits.—These are formed by the alteration and concentration of the manganese in the bedded deposits. The type localities are: Aitemvalasa, Koduru, and Garbham.

3. Replacement Deposits.—These are formed by replacement of the country rock by manganiferous solutions. Type localities are: Devada, Chipurupalle, and Koduru.

Bedded Deposits.—The ore body, consisting mainly of manganese oxides, is medially situated with calc-granulites on either side in Koduru, garnet-sillimanite gneisses in Devada and D'uvvam, and quartz-garnet—sillimanite-graphite gneisses in Sandanandapuram. In all of the type areas the ore body is bedded and is conformable with the associated para-gneisses striking north-west. The ore body, along with the para-gneisses, dips east in most places.

In Koduru the ore body is in close association with the calc-granulites, which are highly contorted forming recumbent folds, measuring 20 feet from limb to limb and pitching NE. In the main pit (No. 19) of the Koduru area there are two ore layers conformable with the calc-granulites striking northwest and dipping to the east at angles of 10° and 20°. These represent a contorted manganese layer once continuous but now separated into two because of the crest being eroded. Further, the ore layer that is generally 20 to 25 feet in thickness, and which normally underlies the calc-granulite, appears reversed in position in the log-diagram. These observations suggest folding and inversion of strata effecting the ore body and the associated calc-granulites.

Garbham is the largest deposit in the district. The ore bed can be traced continuously north west-south east, which is the strike direction of the associated para-gneisses. The open quarry extending to a depth of 300 feet exposed two ore layers roughly 20 to 25 feet in thickness, and these layers are conformable with the associated para-gneisses. Both layers dip 55° N.W. It is most probable that the two seperate layers represent a gently folded single original manganese bed once continuous but now separated due to weathering.

The ore body at Aitemvalasa is conformable with quartz-garnet—sillimanite-graphite gneisses, which strike northwest and can be traced for a mile on either end. In other places of Visakhapatnam the ores are conformable to the para-gneisses striking northeast, which is the general trend of eastern ghat rock types.

Massive Botryoidal Ores.—These ores occur in close association with the above types and may be transported long distances and deposited. This type of ore is very common in Koduru and the ore body is most irregular, massive, and botryoidal in form, and is associated with highly altered gneisses.

Although the general trend of the geological formations in the areas is north west-south east, it may be noted that there are inconsistencies in strike. It is in such structurally disturbed zones that the secondary type of ore is mostly concentrated. These features are more prominent in Garbham where paragneisses, particularly in the northern and southern parts of the area on either side of the ore body, do not show the same trend. This is a clear evidence of slipping of strata along the strike. The Pallapagudi quarries situated one mile north-west of Garbham village represent extensions of the Garbham deposit. The wall rock here is quartz garnet-sillimanite-graphite gneiss with thin layers (about 2 inches thickness) of manganese. Although the manganese layers and the gneisses are generally conformable here, some discomformity is suggested since the plane joining the end of one layer to the end of the other layer contains lenses of chert and traces of manganese (Fig. 3). Though there is no other evidence, the disposition of the two bands may indicate slipping, separating a once continuous band.

Aitemvalasa is another interesting area suggesting dislocation of strata and formation of secondary ores. The contact of the quartzites and the gneisses is unusual suggesting faulting in the dip direction.

Replacement Deposits.—Although these deposits are not economic, those occurring in Devada and Aitemvalasa are of interest. The garnets and pyroxenes of the country rock were gradually replaced by manganese oxides, probably by solutions.

There are also irregular, massive manganese bodies measuring 17 feet long by 5 feet wide, and branching off at the periphery (Fig. 4). The dashed positions in the figure indicate manganese and the white portions lithomarge and clay. The branching of this ore body along the peripheral zone into in-

FIG. 3. A SKETCH OF STRUCTURE OF MANGANESE IN PALLAPAGUDI

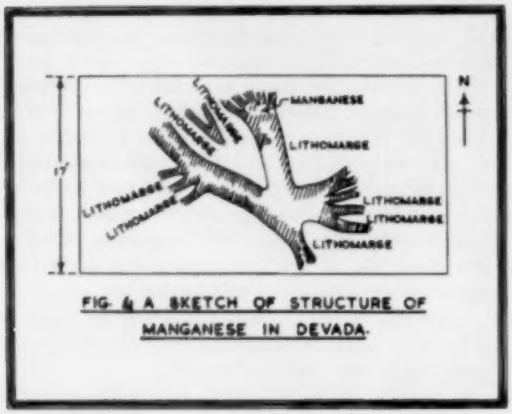

FIG. 4 A SKETCH OF STRUCTURE OF MANGANESE IN DEVADA.

numerable small veins is a conspicuous feature. These veins along the border measure 3 inches to 3 feet in length.

From the above observations, it is suggested that the manganese deposit, which was originally deposited along with the associated para-gneisses, has also suffered severe structural disturbances. The geological mapping in the type area shows much variation in the strike and dip of the ore body and the associated para-gneisses. It appears from the field observations that the deposits of Koduru, Garbham and Aitemvalasa are detached portions of a major plunging fold (Fig. 1B), the nose being near Koduru and the manganese ore body occupying the core of this possible anticline.

The manganese bed, which has been folded, cannot be traced continuously because of the associated faulting, and it is in the fault zones that most of the secondary ore is located. However, it must be mentioned that this in itself is not conclusive unless the intermediate areas in between the type deposits are mapped on a large scale with particular reference to the structural features of the rock types and the ore body.

STRATIGRAPHIC POSITION OF THE MANGANESE DEPOSITS

The Khondalite suite of rocks associated with manganese ores are a part of eastern Ghat formations extending along the east coast of India from Guntur through districts of Krishna, Godavari, Visakhapatnam, and Srikakulam on to Orissa (a distance of 300 miles). Essentially these consist of quartz-garnet sillimanite-graphite gneisses with local variation to calc-granulites on one hand to quartzites on the other. The geological formations mapped in the manganiferous areas of Visakhapatnam and Srikakulam districts show much structural disturbance not only from place to place but also locally. These structural features suggest that the area under study was subjected to great structural disturbances and the manganese ores and man-

ganese-bearing rocks occurring along with the Khondalite suite have also been subjected to the same severe forces. Since no second primary ore body is known down dip, and from the data of the sections (Fig. 5), it would appear that the ore body occupies the core of a possible fold. If so, the manganese silicates and the ore body may perhaps be the oldest in the sequence of strata in this region. Thus it follows that the primary ores forming a part of the Khondalite suite of sediments occupy a definite position in the succession of the aluminous and calcareous sediments from which the Khondalitic and calcareous gneisses have been derived.

Manganese ores in other parts of India range from Jhabua in Central India through Nagpur Balagat in Madhya Pradesh, to as far as Gangapur, and also the states of Mysore and Orissa. In different places, the manganese ores occur in association with the oldest known rocks, namely the Precambrian. Correlation of these distant manganese deposits based on their lithological similarities would be entirely mineralogical and petrographic. The genetic relationship of the various deposits and their correlation would be more appropriate if based on structural and radio-active studies. Structural and radioactive studies of the Precambrian of India was attempted by Holmes (3) who distinguished in the Precambrians a number of orogenic cycles, and and the geological formations associated with these orogenic cycles have characteristic structural trends (4). These two studies distinguished the following three major orogenic cycles in the oldest known rocks of India: Satpuras, Eastern Ghats, Dharwars.

The Satpuras have a general east-west trend, the eastern Ghats show the general north east-south west trend, and the Dharwars show characteristic north west-south east trend. Manganese ores occur with all the above

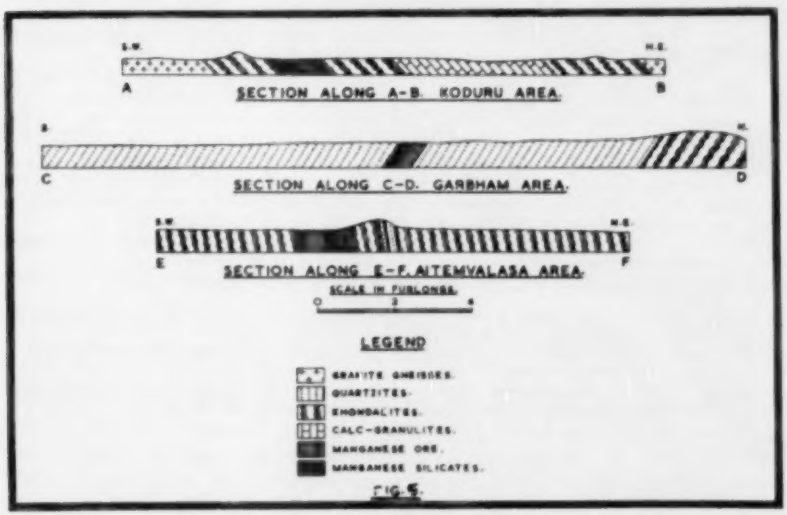

FIG. 5.

TABLE 1

MANGANESE ORE DEPOSITS AND THEIR ASSOCIATED FORMATIONS

Arthur Holmes (3)	Mysore	Koduru	Madhya Pradesh
955 M.Y. Satpura orogenic belt			Sakoli series Sausar series Chilipi Ghats (*Gondites*) Sonawani gangapur series (Gondites and marbles)
1,570 M.Y. Eastern Ghat orogenic		Eastern Ghats (*Khondalites and Manganese ores*)	
2,300 M.Y. Upper Dharwares 2,450 M.Y. (Goldreefs) Dharwarian orogenic belt	Upper Dharwars *Middle Dharwars* *Manganese ores* Lower Dharwars Oldest Archeans		

groups in India suggesting that the various deposits are not contemporaneous in their formation but belong to different periods of deposition during the Archean Era. The manganese ores of the district under study belong to the eastern Ghat period, and those in Madhya Pradesh and Mysore belong to Satpuras and Dharwars respectively. Table 1 summarizes the stratigraphical position of the deposits of Visakhapatnam and Srikakulam districts and its relation to the other lithologically similar deposits in India.

ANDHRA UNIVERSITY,
WALTAIR, INDIA.
Nov. 16, 1959

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SCIENTIFIC COMMUNICATIONS

COMMENTS REGARDING ORE GENESIS AT SILVER REEF, UTAH

RICHARD V. WYMAN

The most recent publication on the geology of Silver Reef is that by Paul Dean Proctor (1) in which he hypothecates an origin of the silver mineralization from the leaching of Triassic volcanic tuffs, and transportation of the metals as sulfates to the seat of syngenetic deposition within the Silver Reef sandstone.

The following comments are intended principally to refute the arguments presented by Proctor, rather than let his work stand uncontested. Additional facts based upon the work of the recent operators add weight to the epigenetic origin of the orebodies from hypogene solutions.

ARGUMENTS FOR SYNGENETIC ORIGIN ANSWERED

On page 121 Proctor lists eleven points that must be considered in any theory of origin. Most of these points as presented tend to favor a syngenetic origin. They are as follows:

1.) The occurrence of silver chloride in association with copper carbonates and minor amounts of uranium-vanadium minerals and some selenium.
2.) The known areal distribution of minor silver and copper content in the St. George basin.
3.) The localization of commercial ore deposits in light colored sandstones interbedded with red sandstone and shales of the Triassic Chinle formation.
4.) The common association of the metallic minerals with plant remains.
5.) The concentration of silver and copper minerals in stratigraphic units within the sandstone member.
6.) The association of silver, and to a lesser extent, copper with clay galls.
7.) The paragenetic sequence of deposition of the different minerals in the deposits.
8.) The absence of the associated intrusive rocks with the mineral deposits.
9.) The lack of silicification, sericitization, typical ore textures, and other accompaniments of hypogene deposition.
10.) The absence of recognizable feeder channels for the different orebodies.
11.) The occurrence of silver- and gold-bearing chalcocite-pyrite concretions in the bentonitic shale 310 feet below the Silver Reef sandstone.

The assemblage of metals described in item 1 should also include iron, which is especially prominent as spongy limonite associated with the uranium ores. Otherwise there is no difference of opinion as to the presence of the metals. The assemblage could fit an epigenetic origin from hypogene solutions just as well.

In item 2 above, Proctor implies a wide areal distribution of metals in the Silver Reef. There are a few other deposits of this type known in the Santa Clara, St. George, and Hurricane areas. However, the deposits are isolated from one another, small, and not necessarily in the same stratigraphic position. In fact, minor amounts of silver and copper are known from the Shinarump up through the Dakota in the general area.

Item 3 is an undisputed fact. The light color, however, crosses bedding planes and spreads out from fractures and jointed areas. The light color described by Proctor as the Leeds Sandstone is also believed to be an alteration phase rather than a sedimentary facies. The relation of alteration of this type to ore mineralization is direct and significant, and can be used as a guide to favorable areas on a district basis, although it is too general a guide to be used for locating specific ore shoots.

Item 4 is only half true. To this should be added, "the occurrence of silver in the absence of plant remains," and "the occurrence of plant remains in the absence of any metals." The experience in the district was that plant remains were not a good indication of mineralization. Much of the silver ore lacks plant remains, and in one case—the 200 level of the Cobb mine—charified plant remains occur unmineralized only a few feet from a commercial silver body that contained no plant remains. Organic material was much more important in localizing uranium, as would be expected from the conditions required for its precipitation as described by Garrels (2).

Items 5 and 6 are explained as the result of selectivity based on structural or chemical favorability. Similar selectivity in limestone sections has been noted in many mining districts where one bed is favored for some reason. In the Silver Reef district, the favored bed is not always in the same stratigraphic position within the sandstone, and there are also instances of several mineralized beds lying over one another.

Item 7, the paragenetic sequence, can be explained satisfactorily on the basis of epigenetic hypogene mineralization.

Item 8 is only partly true. There are no known igneous rocks other than recent basalts in the district. But the huge igneous mass of Pine Valley Mountain lies within 6 miles to the north. This has been described by Cook (3) as a laccolith intruded beneath a blanket of ignimbrites. In many mining districts the granitic mass ascribed as a source of the metal is farther than this.

Nothing is known of the presence or absence of igneous rocks underneath the district. In particular, it is possible that the Virgin Anticline itself may contain a laccolithic mass that has not been exposed by erosion.

Item 9 is not true. A halo surrounding the ore deposits is mildly silicified In particular, the individual quartz sand grains are extended by authigenic overgrowths to form a quartzitic rock. It is notable that the stope backs stand well for this reason. Development of sericite is seen within the ore. At greater distance from the ore alteration in the form of bleaching, hydration of hematite, and removal of iron may be considered as a "normal" accompaniment of ore deposition.

To use the apparent lack of "typical" ore texture as supporting the syngenetic theory in an un-typical deposit is not a logical argument.

Item 10 is not true. In mining the Big Hill orebodies, the relationship of ore to feeders was clearly shown. There was even a zoning of metals away from the feeders, which was quite convincing.

The feeder channels consist of strong fractures of small displacement of a few inches or a foot. Minor distribution was along joints from that introduced along the feeders.

In the Big Hill mine the zoning is as follows: A central zone of high-grade uranium and much limonite iron surrounded by a zone of silver-bearing uranium ore. Farther out and surrounding this zone is a broad area of silver ore with little or no uranium. This gradually decreases in grade to an economic limit. There is some increase in copper in the peripheral area. In following the faults that are described as feeders, as they leave the uranium area they are still distinctly related to mineralization, and contain high-grade silver ore on both sides, decreasing outward until another feeder is approached.

A very prominent feeder is located on the Buckeye Reef where all of the mined orebodies appear related to it. I refer to the fault illustrated by Proctor in Plate VIII, page 58. This fault was even stoped as a vein within the Buckeye Mine.

On the White Reef, a strong system of through going fractures is related to the Cobb-Newton mine, and another to the Barbee-Walker. On the East Reef each of the several small ore showings has a similar structural locus.

Item 11 describes the concretions on Fire Clay Hill. It should be noted that this hill is in the center of the eroded Leeds Anticline, and only a few hundred feet from some of the biggest producers of the district. It is not surprising to find mineralization there. In fact, this can be used as an argument favoring a hypogene origin of the ore, as there is no evidence that these concretions are syngenetic.

Of the above comments, the most important favoring an epigenetic origin are those concerning the alteration of the sandstone, and the presence of structures to channel the ore solutions. Additional structural controls of deposition have been noted since the earliest days of the camp; some of them are:

1.) Location of the district on the nose of the Virgin Anticline.
2.) Location of the principal producing area of the district on the Leeds Anticline.
3. Location of orebodies underneath clay beds, and in highly fractured areas, especially near faults of small displacement.

The control of mineralization by structures that were formed during Laramide or Tertiary time is sufficient evidence that the orebodies as they appear today are epigenetic. These same structural controls were used successfully to locate unoxidized black uranium and sulfide mineralization below the zone of vadose circulation, which throws still greater doubt upon the theory that these bodies were formed by secondary enrichment of a widespread low-grade mineralization.

ASH LEACH THEORY

Proctor states that the silver was derived from the leaching of the Bentonitic Shale member of the Chinle. On page 21 he lists analyses of these shales. The two highest assays were 0.10 oz Ag and the rest were "trace" or none. All samples were taken within the mining district. The thickness of the bed is 10 to 13 feet.

If the tiny amount of silver present were leached with 100 percent efficiency and moved by surface streams in solutions and reprecipitated 100 percent within the Silver Reef sandstone, then in order to account for the quantity of silver from recorded production plus that remaining in low-grade ores and dumps, a total of 6 square miles of the shale would have had to have been leached. All of these conditions are highly improbable.

In addition, the fact that the Silver Reef itself averages more than 0.10 oz Ag per ton, and is 100 feet or more in thickness, calls for the additional leaching of 10 square miles of the bentonitic shale for each square mile of the Silver Reef sandstone, assuming complete leaching.

There is no evidence that the bentonitic shales normally contain as much as 0.10 oz Ag, as again, all samples were taken within the mineralized district, and only 310 feet below the known "reef" mineralization. Of the 6 samples, two had no silver, two had a trace and two had 0.10 oz Ag. This is very little upon which to base a theory of genesis.

If the bentonitic shales formerly existed in larger volumes, then there should be evidence of the presence of large quantities of redeposited bentonite within the Silver Reef. In fact there is none, or so very little that it is of distinctly minute importance.

CONCLUSION

The theory of genesis of the Silver Reef mineralization from a syngenetic process is doubtful on the basis of the evidence. The theory of genesis from the leaching of underlying bentonitic shales appears impossible from a logical approach, as well as from the field evidence.

An epigenetic origin for the orebodies fits the facts, and is especially substantiated by the presence of related alteration and a relation of orebodies to post-Chinle structures. A hypogene origin for the ore solutions appears most logical in view of the epigenetic origin, presence of igneous activity in the general vicinity, and stratigraphic distribution of the known mineralization. Solutions in their migration were controlled by permeability and ore deposition by chemical favorability of the beds as well as structure.

The ore solution must have been capable of carrying silver, copper, uranium, vanadium, gold, selenium, and sulfur. Further reconstruction of the nature of the ore solution would be a worthwhile step in the study of the ore genesis.

ACKNOWLEDGMENTS

The ideas advanced above have been the opinion of the writer for a number of years, and were the result of geologic studies at Silver Reef during

the years of 1954 to 1957 when employed by Western Gold and Uranium, Inc. as Chief Geologist and General Superintendent.

I wish to acknowledge the stimulating conversations on the subject with other geologists who have been over the ground with me and encouraged me to record my observations for publication.

INTERMOUNTAIN EXPLORATION COMPANY
ST. GEORGE, UTAH
April 4, 1960

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Economic Geology
Vol. 55, 1960, pp. 840–847

DISCUSSIONS

SOME GEOCHEMICAL CONSIDERATIONS ON LEAD-ISOTOPE DATING OF LEAD DEPOSITS

Sir: In a recent issue of this Journal (vol. 54, p. 951–953, 1959), R. D. Russell has taken issue with certain points in my recent paper on lead isotopes (ECON. GEOL., vol. 54, p. 130–135, 1959). In the first part of his discussion he refers to the term "fractionation" claiming that my usage is misleading. His argument on this point is partly a semantic one, but it also reflects a difference in viewpoint.

I am fully aware of the physico-chemical definition of fractionation as it is used by Dr. Russell to describe the phenomena whereby isotopes may be separated during chemical and physical processes because of differences in their masses. This definition in my opinion is too narrow when considering the geochemical processes that concentrate lead isotopes in lead deposits.

I have, therefore, used the term "fractionation" in its broadest geochemical sense in my paper. My use of the term includes the true fractionation referred to by Dr. Russell as well as those other processes which lead to the separation of the lead isotopes because of their different origins and binding relationships. In this I feel I am justified because the process I postulate for the concentration of lead deposits, namely a secretion mechanism, involves mobilization of lead from its bound sites in silicates, sulphides, etc., adsorption -desorption phenomena, and migration by diffusion. It is during these particular processes that true fractionation would take place.

Dr. Russell is rather dogmatic on the point that true isotopic fractionation of lead isotopes by physico-chemical processes has never been observed in nature. I do not know upon what evidence he bases this conclusion because there are no detailed field or laboratory studies yet published that give any information on this particular problem. There is for instance no detailed knowledge of the molecular binding properties of individual lead isotopes, nor do we have any information on the relative mobilities of individual lead isotopes during diffusion processes in rocks or natural solutions. Until we have this knowledge no definite statements can be made.

On theoretical grounds, however, there is reason to suspect that physico-chemical fractionation of lead isotopes may take place. It is well known that the heavier uranium isotopes can be fractionated by gaseous diffusion processes as in certain atomic plants. Admittedly these processes involve much recycling, but they are entirely analogous to the situation which must exist in the diffusion of lead isotopes through rocks during metamorphism and ore deposition. There are also theoretical reasons, for suspecting that adsorption-desorption processes may fractionate lead isotopes, and also that individual lead isotopes have slightly different and perhaps selective molecular binding properties. Because of these considerations I lean to the view that some physico-chemical fractionation of lead isotopes is a possibility during the concentration of lead deposits.

In his discussion of the use of lead isotope analyses in dating, Dr. Russell says that they are not used to indicate the age of a lead deposit. Rather he maintains that the age value refers to the time the lead was separated from its source rock. This fine distinction is, however, not made clear in most published data, and as far as I can see is of minor significance. Geologically speaking, and assuming either a secretion or magmatic origin for lead deposits, there is little difference in age between the time the lead was separated from its source rock and its deposition in a lead mineral, perhaps 50 to 100 million years at most, an interval of time which is not within the precision of the lead dating method.

R. W. BOYLE

GEOLOGICAL SURVEY OF CANADA,
OTTAWA, ONTARIO,
Jan. 26, 1960

ANOMALOUS LEADS AND THE EMPLACEMENT OF LEAD SULFIDE ORES—ERRATUM

Sir: In our recent paper "Anomalous leads and the emplacement of lead sulfide ores" (ECON. GEOL., vol. 54, No. 4, p. 588–607) we inadvertently included the Keymet and New Larder U mines, both of New Brunswick, in our Table 2 "Conformable deposits." It was in fact our intention to include only the Brunswick Mining and Smelting (B.M. and S. No. 6) and Anacon Leadridge (B.M. and S. No. 12) deposits among the "Bathurst" group. The inclusion of the other two occurrences was a semi-clerical error, and arose as a result of all four occurring in the "Bathurst" area of New Brunswick, and hence all having the common prefix "Bathurst —" in our laboratory lists.

Of the two deposits concerned, the Keymet seems clearly of vein type (see McAlister, A. L., in "Structural Geology of Canadian Ore Deposits," Seventh Commonwealth Mining Congress Symposium (Volume p. 494) and, if our theory is correct, must be regarded as one of the occurrences of uncontaminated vein leads which so far have appeared in all of the epigenetic groups investigated by us. This has been considered fully in our Discussion, and is illustrated clearly in our Figure 5. As the Bathurst area is not known to contain notable quantities of old radiogenic matter, and is in fact largely composed of andesite-basalt lava, pyroclastic rocks and their derivatives, such occurrences must be regarded as normal and to be expected on the basis of our work.

We have no detailed information on the New Larder U occurrence.

R. L. STANTON

DEPARTMENT OF GEOLOGY,
UNIVERSITY OF NEW ENGLAND,
ARMIDALE, NEW SOUTH WALES
AND

R. D. RUSSELL

GEOPHYSICS LABORATORY,
DEPARTMENT OF PHYSICS,
UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, B. C.

DISTRIBUTION OF WITWATERSRAND URANINITE

Sir: In Volume 54, pp. 1316–1320, of this journal, Professor Davidson has once again set out certain sedimentological and geochemical criteria in support of the hydrothermal origin of Witwatersrand ores which he so staunchly champions. He points out (p. 1317) that the fine grain size of the uraninite does not support the contention that under normal sedimentary conditions this mineral, because of its high specific gravity, should concentrate along with the coarsest detritus, an argument put forward by Ramdohr (1, 2). Davidson quotes my figure (3) for the grain size of Witwatersrand quartzites (1.4 mm) derived from a suite of specimens from the Upper Division of the System on the East Rand, and on the basis of Stokes formula shows that no preferential concentration of uraninite should occur in the conglomerates. He goes on to ask (p. 1317), "Why then, if the uraninite is detrital, should it preferentially accumulate in high concentration solely or principally within the conglomerates? That it does so, contrary to the elementary principles of sedimentation, is an eloquent demonstration that it cannot be alluvial."

It would perhaps be trifling to recall that Stokes formula does not apply to materials of grain size such as are found in Witwatersrand sediments. Modifications of the formula to cover these coarser grades would in all probability not substantially weaken Professor Davidson's argument, but it is clear that natural conditions do not always simulate the ideal "settling in water" requirement of the formula. Rittenhouse (4, p. 1764), for example, has shown that in bedload transportation departures from the hydraulic equivalent size concept result from erosion or "picking-up" factors, which are as yet imperfectly understood. Until experimental work has shown us more about the behavior of small rounded heavy particles in a turbulent sedimentary setting we should apply somewhat idealized formulae with caution.

A more serious weakness of Professor Davidson's argument relates to the lack of critical consideration of possible sedimentary settings within which the ore-bearing conglomerates accumulated. This is a speculative field but a few observations may not be out of place.

One of the outstanding characteristics of Upper Witwatersrand quartzites is their extraordinarily coarse grain size. If we can accept the figure of 1.4 mm (3) as being representative, we are presented with a sedimentary system of unusual coarseness. Furthermore the grains comprising the quartzites are mostly single crystals and show little rounding (3, p. 33). It is clear that they were derived from a local coarse grained primary source of quartz. The rocks themselves appear poorly sorted (recrystallization of matrix materials partly obscures this feature), are massively bedded and commonly cross-stratified, all of which suggests that the basin was filled rapidly from local sources. The conglomerates, on the other hand, particularly the mineralized ones, are well sorted and are outstanding for their continuity despite small thickness. They consist mostly of very well rounded durable pebbles and in fact indicate long transport under conditions of sustained equilibrium that permitted the development of extensive gravel sheets.

There are indications, therefore, that the conglomerates and quartzites were derived from different sources. The coarse grained quartzites suggest the interpretation that the basin was bounded by faults and that during much of Upper Witwatersrand time drainage was effectively disintegrated by recurrent dislocations. At intervals through drainage must have been established and master streams introduced materials from sources outside the immediate confines of the basin. At these times, apart from gold and uranium, platinoids and chromite were introduced, the latter indicating ultramafic sources evidence for which is lacking in the monotonous quartzo-feldspathic debris that makes up the bulk of the Upper Division of the System.

Professor Davidson's argument, therefore, that because uraninite is concentrated in the conglomerates we are provided with an eloquent demonstration that it cannot be alluvial, is not necessarily effective. The statement is an illogical extension of his probably correct refutation of Ramdohr's assertion that "a mineral of very high specific gravity must, in his view, preponderate in the coarsest detritus."

A. O. FULLER

GEOLOGY DEPARTMENT,
UNIVERSITY OF CAPE TOWN,
SOUTH AFRICA,
February 1, 1960

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ALTERATION OF ILMENITE AND "ARIZONITE"

Sir: In a recent article in ECON. GEOL. (v. 54, p. 720) Flinter discusses the alteration products of Malayan ilmenite. He has reported for the first time the occurrence of pseudobrookite in the alteration products. This occurrence is also substantiated by our work (ECON. GEOL., v. 54, p. 915). However, I find it difficult to agree with his conclusion that the alteration product of ilmenite is arizonite, and with his suggestion (p. 729) that the term "arizonite" be "retained to indicate the third phase (of alteration), so far not found in Malaya, in which recrystallization has occurred and a well defined X-ray powder pattern obtained. The name would be analogous to the terms limonite, bauxite or gummite and would represent an end-product consisting of titanium oxides (rutile and/or anatase and/or brookite) and iron oxides, although theoretically there may be no iron oxides."

Leucoxene is considered as a generic name for such alteration products, and arizonite represents a finite chemical compound, ferric metatitanate.

Arizonite has a distinct X-ray powder pattern quite different from that obtained by Flinter or by us for leucoxene which is a mixture of either rutile, hematite, and pseudobrookite or rutile and/or anatase and hematite. The fact that the chemical analyses yield percentages of Fe_2O_3 and TiO_2 required for arizonite, is not enough justification to call the products arizonite. The alteration product is not a single compound but a mixture.

Also there is no evidence to support his conclusion that pseudobrookite is unstable at high temperatures. All previous work as well as our recent work on the system Fe_2O_3–TiO_2 (J. Amer. Ceram. Soc., v. 42, p. 399, 1959), confirm the stability of pseudobrookite. Momin (unpublished work) has found that pseudobrookite melts at 1,495° C, and there is no evidence of any decomposition below that temperature.

The absence of pseudobrookite in the fully altered grains is probably due to the loosening and eventual falling out of the pseudobrookite grains. This would explain the co-occurrence of pseudobrookite grains in substantial amounts in such sands as found by us (ECON. GEOL., v. 54, p. 913), as well as the large indentation marks and grooves found on the fully altered leucoxene grains.

M. D. KARKHANAVALA

BOMBAY, INDIA,
February 9, 1960

THE WILLEMITE–HEMIMORPHITE RELATIONSHIP

It was F. H. Pough (1) who first pointed out that willemite (Zn_2SiO_4) is a mineral most characteristic of the oxidized zone of certain zinc sulfide deposits and that its development in the well known Franklin Furnace occurrence is exceptional. Recent papers by Taylor (2) and Verwoerd (3), describing willemite from Broken Hill, Northern Rhodesia and Abenab West, South West Africa, clearly indicate a secondary mode or origin with the zinc silicate forming by the direct replacement of primary zinc sulfide. Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) is likewise a common product of the oxidation of sphalerite in the presence of silica. A problem that immediately arises, therefore, is why the anhydrous silicate willemite should sometimes develop in preference to the hydrous silicate hemimorphite. This problem was, in fact, discussed earlier by Pough (1) who considered that arid climatic conditions together with the high concentration and possibly special composition of the oxidizing solutions were responsible for the development of willemite, through conrtibutory factors were thought to be somewhat elevated temperatures and pressures brought about by the depths at which oxidation had taken place. Taylor (2) and Verwoerd (3) have echoed similar views, both authors emphasizing the effects of prolonged weathering under hot arid conditions.

It may, perhaps, be of value to re-examine this question in the light of experimental work carried out by Roy and Mumpton (4) in the system

ZnO-SiO_2-H_2O, the results of which have recently been published in this journal. Their curve of particular interest is that for the reaction.

$$\text{Hemimorphite} \rightarrow \text{Willemite} + H_2O$$

which is reproduced in Figure 1. The dehydration curve, though necessarily pressure dependent, would intersect the temperature axis at around 210° C for low-water vapor pressures, a temperature considerably higher than that to be anticipated even in the deepest portions of an oxidized zone. It is possible, however, to make a partial reconciliation between experimentally determined temperatures and those thought to exist in a natural mineral system. For purposes of discussion, reference is made to the important lead-zinc-vanadium deposit at Berg Aukas, together with other willemite occurrences in the Otavi Mountains of South West Africa.

At the Berg Aukas Mine exploratory diamond drilling has indicated surface oxidation to depths in excess of 2,100 feet. Willemite, cerussite, smithsonite and descloizite are all prominently developed and microscopic examination reveals that willemite and smithsonite have formed by direct replacement of sphalerite, while cerussite owes its origin to the replacement of galena. Associated descloizite crystals may form a coating on willemite-cerussite ore and the vanadium mineral is clearly a late phase of the oxidation process. The replacement textures observed in these deeper drill intersections are in no way different to those noted in the upper levels of the Berg Aukas mine and are very similar to those previously described by Taylor (2) and Verwoerd (3). Moreover, the host dolomite rocks show prominent caverniza-

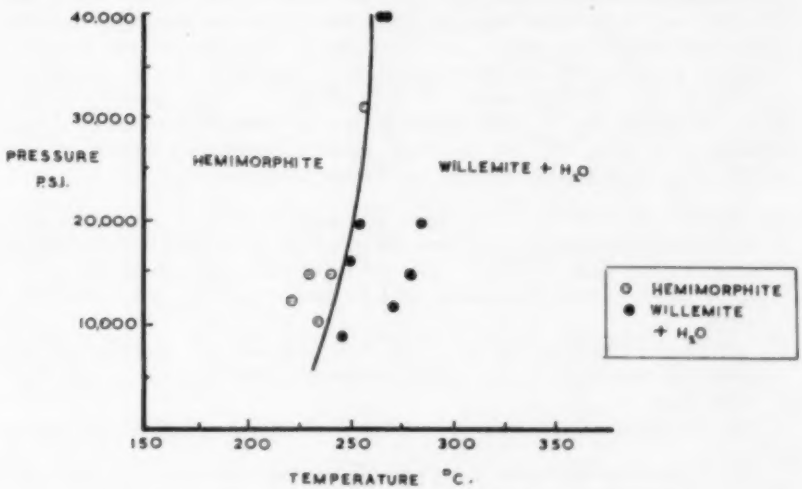

FIG. 1. The hemimorphite-willemite dehydration curve after Roy and Mumpton (4).

tion which has occurred since the sulfide mineralization to at least 1,600 feet below the present surface level. Many of these cavities, which may be open or partly filled with dolomitic mud, have been formed along zones of prominent sulfide mineralization so that the walls of the cavities are commonly made up of sphalerite-galena ore now largely oxidized to willemite, cerussite and descloizite. These cavities point to a period of deep water circulation under oxidizing conditions. Geological evidence suggests, however, that a regional water table did not exist to such depths, rather that there were certain zones, permeable to water, along which circulation was at a maximum. Under hot, arid conditions a surface temperature of around 35° C is not excessively high. Assuming a geothermal gradient of 1° per 90 feet it might be anticipated that temperatures of the order of 60° C would be met with at a depth of 2,100 feet. It is to be expected that slowly circulating waters in an arid region would be in close thermal equilibrium with the surrounding rocks, hence the temperature of such solutions would not deviate greatly from this figure. It must be clearly borne in mind, however, that significant concentrations of willemite occur close to surface and in the upper levels of the Berg Aukas Mine where a marked rise in temperature above that of 35° C cannot be postulated (in this respect the prominent surface outcrops of willemite at Abenab West (3) and Baltika (5) are also noteworthy). The above remarks merely suggest that a marked rise in temperature doubtless occurs in the deeper portions of an oxidized zone but that the temperature factor alone cannot be the sole explanation for the development of willemite.

Referring again to Roy and Mumpton's hemimorphite-willemite dehydration curve, it will be noted that their work was carried out under varying total pressures of pure water vapor. In the natural system under consideration, not only is the water vapor pressure likely to be extremely low but the water itself will not be present as a pure phase. Both factors will have the effect of lowering the dehydration curve temperatures in the natural as opposed to the artificial system. The problem has been more rigorously stated by Thompson (6) who shows that experimentally determined dehydration curves give only the maximum possible transition temperature, the actual temperatures being effected by, among other factors,

a) Whether the fluid phase is a pure component or not. If not, the chemical potential or partial molar free energy of the component in the mixture must be less than the molar free energy of the pure component at the same pressure and temperature. This implies lower transition temperatures.
b) Whether the pressure acting on the fluid phase is less than that of the solid. If such is the case, lowering of the transition temperature will also take place.
c) Whether the system is open or closed to any of the components concerned.

In the environment under consideration, all three factors are favorable to the lowering of the hemimorphite-willemite transition below that of experimentally determined temperatures. In particular, oxidation of sphalerite

under arid climatic conditions may take place, at certain periods of the year, in a system deficient with respect to water. Yet there is at present no means of gauging the magnitude of such a lowering. If the factors mentioned above could lower the hemimorphite-willemite transition to within the range 35–60° C, then the presence of abundant secondary willemite is readily explained for those areas possessing appropriate chemical and climatic features. On the other hand, if it is unlikely that the transition temperature could be lowered significantly below say 150° C, then strong evidence for a disequilibrium state is obtained. If such be the case, then the willemite at Berg Aukas, Abenab West and Broken Hill has formed metastably.

It is of interest to note that Roy and Mumpton's dehydration curve was obtained using amorphous gel mixtures as starting materials for their runs. They found, however, that natural hemimorphite showed no evidence of decomposing to willemite at a temperature of 600° C and natural willemite, when subjected to hydrothermal treatment at temperatures below those of the dehydration curve, showed no evidence of being transformed to hemimorphite. Evidently, therefore, the transition between the two minerals is a sluggish one with ample scope for the development and retention of metastable phases.

Additional experimental work in the system ZnO-SiO_2-H_2O at low temperatures (35–70° C) is required. Even if willemite forms metasably under certain conditions, a knowledge of the chemical factors necessary to produce willemite may shed some light on the environment of deposition at the localities described. That the conditions necessary to produce willemite did not uniformly apply over the whole Otavi Mountains region is shown at the Harasib 11 N. prospect, where hemimorphite and not willemite is the sole secondary zinc silicate mineral.

N. L. MARKHAM

GROOTFONTEIN
S. W. AFRICA
April 4, 1960

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Economic Geology
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REVIEWS

Our Mineral Resources. By CHARLES M. RILEY. Pp. 338; figs. 102. John Wiley & Sons, New York. Price $6.95.

As this book is not in essence another statistical or political treatise, its subtitle, "An Elementary Text in Economic Geology," gives a better idea of its content than does the main title. Its avowed purpose is to supply the "needs for an elementary course in economic geology." For "a cultural course in earth science" it seems admirably adapted, but as "an introduction to a curriculum for the training of a professional geologist" the subject matter could be taught to better advantage at a more advanced level.

The book embraces the wide field of metallic and non-metallic mineral deposits with a good balance of pages—186 and 109 respectively—devoted to the two classes. The section on "Non-metallic Mineral Resources" includes, along with the usual topics, an interesting chapter on gems and 15 pages devoted to the most valuable resource of all, ground water.

Presenting the facts and theories of mineral deposition to readers little versed in either chemistry or geology is not a simple assignment. If it is necessary to explain what magma is, and the difference between a gravity fault and a thrust fault, it will hardly be possible to go far into the controversial aspects of ore deposition. Yet, it is not possible in honesty to side-step them. Toward meeting this challenge the author has taken a good middle ground. In his simplified classification of ore deposits he has elected to follow orthodox theory, including the magmatic-hydrothermal hypothesis, while not neglecting to mention less conservative alternatives such as the source-bed theory, neolateral secretion (sic), and concentration by wet or dry diffusion. In describing each individual deposit he presents the most generally accepted theory, points out any alternative ideas, and usually does not hesitate to state his own preference. As he truly states in his introduction, "the limited space and elementary level of this book prohibit a thorough debate of these ideas."

A short book covering such a wide field also poses problems in deciding what deposits to describe. In general the selection is good and includes those of the greatest geological and economic interest with timely attention to postwar developments, such as the iron ores of the Quebec-Labrador trough and Cerro Bolivar, with mention even of the new Thompson-Mystery-Moak Lake nickel area. As against this there are some rather startling omissions. Of the world's three great lead districts, only Sullivan, B. C. is described. "Another lead-producing area in southeast Missouri" gets only the six words just quoted, and the richest of them all, Broken Hill, goes unmentioned. Among copper deposits, Northern Rhodesia is represented only by a statistic. But these gaps, most of them in the foreign field, may not give serious pain to readers interested in "our" mineral resources.

Interestingly written and well illustrated by fresh photographs and unhackneyed line-cuts, it is good reading not only for students but for any layman with an interest in geology.

HUGH MCKINSTRY

Osnovnye Cherty Magmatizma i Metallogenii Chatkalo-Kuraminskikh Gor. [General Outlines of the Magmatism and Metallogeny of the Chatkalsk-Kuraminsk Mountains.] Edited by Kh. M. Abdullaev. Pp. 289. Uzbek Academy of Sciences, Tashkent, 1958. Price 21r. 75k.

The Kuraminsk Mountains are a spur of the Chatkalsk group in the western Tien Shan, and include the Hercynian granodiorite batholith of the Kara Mazar range, forming the boundary between north-western Tadzhikistan and eastern Uzbekistan. Even before the war upwards of 400 separate deposits of non-ferrous ores were known here, the most important containing silver-lead and gold for which some of them had been worked since the tenth and eleventh centuries. In mediaeval times there was a relatively large mining industry, widely known throughout the Mussulman world; and silver talismans of Kara Mazar origin formed part of the spoils that the Crusaders of western Europe looted from Islam. The metallogeny is of Variscan age, and is in many ways comparable to that of the Erzgebirge.

In this new work Professor Abdullaev and eight associates summarize the results of recent explorations for polymetallic mineralization, including the ores of silver-lead, copper, cobalt, bismuth, arsenic, molybdenum, tin and tungsten (mainly scheelite). Embracing a considerable wealth of chemical analyses of rocks and other details, their monograph comprises five main chapters on the geology, the magmatism, the relation of metallogeny to diabase dikes (a topic dealt with more fully in Abdullaev's book *Daiki i Orudenenie* of 1957), and the metallogenetic processes. The metallization is divided into the following phases: (a) pre-batholithic, principally disseminated Pb, Zn, Cu ores in Devonian sediments; (b) batholithic, with Be, Mo, Sn pegmatites, greisens, magnetite skarns, and skarns with scheelite, molybdenite and cassiterite; (c) major intrusions and dikes, again with polymetallic skarns and with hydrothermal veins; and (d) fluorite-polymetallic veins, including pegmatites, skarns, greisens and hydrothermal lodes reputedly of Upper Carboniferous age, and another suite of lodes of Lower Triassic age. A special study has been made of wall-rock alteration. Uranium is not mentioned, although pre-war literature refers to minor uranium mineralization at Taboshar and Sarym Sakhly, Andrasman, and elsewhere in the Kara Mazar.

C. F. Davidson

University of St. Andrews,
Scotland.
April 8, 1960

Soupis periodik geologických věd. [Index of Periodicals in Geological Science.] Compiled by Josef Lomský. Pp. 500. Czechoslovak Academy of Sciences, Prague, 1959. Price, 31 crowns ($4.50).

This volume bears the sub-title *Periodica geologica, palaeontologica et mineralogica*. It comes as somewhat of a shock to learn from it that the total number of geological periodicals and serials in the world, including those which have ceased publication, is not less than 3,582! With great diligence the author has listed alphabetically all such journals and continuing works, current and closed, giving full and abbreviated titles; and in indexes he also furnishes cross-references under subject (e.g. petrography) and place of publication. Czech transliterations and translations are supplied for works in foreign alphabets (such as Russian and Georgian) and in ideographs (Chinese, Japanese), but titles in western European tongues are printed as published. The journals of the national academies, museums,

and comparable scientific institutions are not included except where they comprise a separate geological series; and unfortunately most important mining serials are also left out, even those made up largely of geological contributions. Other omissions noted are *American Journal of Science, Prospection et Protection du Sous-Sol, New Zealand Journal of Geology and Geophysics, Proceedings of the Geological Association of Canada,* and *Memoirs of the Wernerian Society;* and a few works included, such as *Devonian Year Book* (London), are not geological at all. But sins both of omission and commission cannot be wholly avoided in a reference work of this kind; and while the text might have benefitted somewhat from Western editing, it will prove of considerable value to geological librarians throughout the world, particularly in connection with the publications of the Communist countries.

C. F. DAVIDSON

Cours de Cristallographie, Vol. II, Cristallographie physico-chimique. By R. GAY, Professeur à la Faculté des Sciences de Bordeaux. Pp. 232; figs. 151. Gauthier-Villars, Paris, 1959. Price, f. 2900 ($6.17).

This is the second volume of four. The first has already been reviewed (ECONOMIC GEOLOGY). This second volume completes the course for most mineralogists and should certainly be used in conjunction with the first. This volume has chapters on the following subjects: thermodynamics of crystals, specific and latent heats, diffusion of atoms in a crystal, surface phenomena, polymorphism, isomorphism and solid solutions, aging of solid solutions (order-disorder transformations, precipitation of new phases within solids), process of crystallization, twins and fibrous and epitaxial associations of crystal grains, and corrosion.

It would seem very reasonable for many to use it as a reference book, even though it might be inconvenient as a textbook where French is not the language of the classroom. Lack of an alphabetical index (there is a rather detailed table of contents instead) makes this book, unlike volume 1, less useful than some others as a reference, however.

Professor Gay's four-volume set, when complete, will be a remarkable and useful series. Perhaps the last volume will contain an adphabetical index to the whole series.

H. WINCHELL

SHORT REVIEWS OF NEW RUSSIAN BOOKS

Problemy Rudnykh Mestorozhdenii. [Problems of Ore Deposits.] Edited by G. A. SOKOLOV. Pp. 513. Inostranizdat, Moscow, 1959. Price, 34r. 40k.

The Fiftieth Anniversary Volume of ECONOMIC GEOLOGY, published in 1955, was translated into Russian soon after it appeared and was marketed in the U.S.S.R. during 1958. This first Russian edition (which the reviewer has not seen) was rapidly exhausted; but the present volume, comprising translations of the twelve papers that form Part I of the English text, is said to follow the earlier printing without change. Apart from the omission of some references to the financial organization of ECONOMIC GEOLOGY, "of no interest to Russian readers," the translation meticulously follows the original. One of the few editorial footnotes confuses A. M. Bateman with J. D. Bateman. The standard of production is high, the 533 pages of the English text occupying 508 pages in Russian. As is usual with works issued by the Publishing House for Foreign Literature, the size of the edition is not stated.

Atlas Vulkanov SSSR. [Atlas of the Volcanoes of the U.S.S.R.] Compiled by A. E. Svyatlovskii. Pp. 175 + 2 maps. 29 × 36 cm. Academy of Sciences, Moscow, 1959. Price 38r. 50k.

Although not concerned with economic geology, this prestige publication depicting the active and recent volcanoes of the Soviet Union merits a notice since it will form a worth-while addition to any geological library. The active volcanism of the U.S.S.R. mainland is confined to Kamchatka, where of just over 100 major volcanoes which have erupted during and since the Quaternary period 13 have been active in historical times and 14 are in a dormant, solfataric, state. In the mountains of the Caucasus strong Quaternary volcanism died away in post-glacial times, but the structure of many eruptive centres such as Kazbek and Elbrus is still excellently preserved. The atlas illustrates these two volcanic provinces in close on 300 photographs, mostly taken from the air, accompanied by a brief but competent text in Russian and (in an abridged form) in English. A companion volume dealing with the volcanism of the Kurile Islands is in course of production.

Kurs Mineralogii. [Course in Mineralogy.] By E. K. Lazarenko. Part I, General Mineralogy. Pp. 286, figs. 220, 1958. Price, 6r. 80k.

Part II, Systematic Mineralogy. Pp. 654, figs. 609, 1959. Price, 13r. 40k. University Press, Lvov. (Ukrainian only.)

Professor Lazarenko is well known to western mineralogists as the editor of the important Mineralogical Magazine (*Mineralogicheskii Sbornik*) of Lvov University and Lvov Geological Society, which has appeared annually over the last twelve years in numbers of up to 500 pages each. His introductory course in mineralogy for geological students in State universities is in three volumes, dealing respectively with general and systematic mineralogy, and (not yet published) the mineralogy of rocks and ore deposits. The first, general, part is particularly interesting in view of the very broad basis of its instruction at an elementary level, and the second volume also is wide in scope and well illustrated. Teachers who are not deterred by difficulties of language will find in these inexpensive works some instructive data and diagrams foreign to Western text-book literature.

Materialy po Geologii Poleznykh Iskopaemykh Yakutii. [Contributions to the Economic Geology of Yakutia.] *Trudy Yakutskogo Filiala A.N.S.S.S.R.*, Sbornik No. 4 [Trans. Yakut Filial, Academy of Sciences of the U.S.S.R., Collection No. 4.] Pp. 200. Moscow, 1959. Price, 12r. 90k.

Three of the ten papers in this collection are concerned with Yakutian diamonds, embracing respectively a study of the petrology of the kimberlites and their xenoliths, a review of the mineralogy of the pipes, and a report on the morphology of the diamonds. Much of this is a re-write, with many corrections, of chapters in the book *Almazy Sibiri* (see Economic Geology, v. 53, p. 220) published two years previously. Some of the illustrations in the earlier work are here reprinted a little larger than before but reputedly with the same scale of magnification: if we are to believe both texts the diamonds must have grown since 1957! It is strange that in the account of the mineralogy of the deposits, sent to press in May 1958, no mention is made of the discovery of natural moissanite late in 1956, a circumstantial description of which has been given elsewhere (*Doklady Akad. Nauk*, v. 115, p. 1189, 1957). Other papers in the collection deal with Yakutian coal deposits and with wall-rock alteration alongside stanniferous sulfide veins.

Olovonosnost' Tsentral'nogo Kazakhstana. [Tin-bearing Formations of Central Kazakhstan.] By G. B. Zhilinskii. Pp. 212, figs. 52. Kazakh Academy of Sciences, Alma Ata, 1959. Price, 14r. 90k.

Tin-bearing pegmatites, greisens, and a few tin-bearing skarns are associated with late Caledonian and late Hercynian granites in the middle of the Central Kazakhstan polymetallic province and along its north-western margin. There are many small, derived placers of which the size and grade are described in some detail. In this pioneer study of the economic geology of the deposits it is concluded that the role of tin in the metallogenesis is relatively small, giving only minor potentialities for production. In 1956 this was only 1.8 per cent of the total Soviet output. The most promising prospects are in stockworks of quartz-cassiterite veins in granite, with wolframite and some sulfides (especially molybdenite and bismuth minerals), giving an overall grade of 0.2 percent and reserves of around 3,000 tons of tin. The tin content of specimens of mica from a cassiterite-magnetite skarn is as high as one percent.

Obshchaya Geologiya. [General Geology.] By O. K. Lange, M. F. Ivanova, and N. B. Lebedeva. Pp. 252, figs. 132. Gosgeoltekhizdat, Moscow, 1958. Price, 6r. 70k.

This poorly produced textbook, approved by the Ministry of Geology for use in higher schools for geological technicians, is uninspired and undistinguished. It merits a notice for containing what is surely one of the biggest propaganda misstatements in scientific literature: "Even in Western Europe, which is very small in comparison with the territories of the Soviet Union, the geological maps are much less detailed than in the U.S.S.R.!"

Geologiya Zheleziste-Kremnistykh Formatsii Ukrainy. [Geology of the Siliceous Iron Formation of the Ukraine.] By N. P. Semenenko and others. Pp. 688, pl. 17, figs. 82. Ukraine Academy of Sciences, Kiev, 1959. Price, 31r. 85k.

In a large work almost wholly occupied by local detail there is only a very brief discussion of the genesis of the deposits, which are associated with a spilitic volcanism, and of their metamorphism.

Istoriya Geologicheskogo Issledovaniya Sibiri. [History of the Geological Investigation of Siberia.] Period V, 1918–1940. Part 9, *Obzor Literatury* [Review of the literature]. By V. A. Obruchev. Pp. 199. Academy of Sciences, Moscow, 1959. Price, 13r. 45k.

The earlier half of the period dealt with in this review (1918–1940) is poorly represented in most Western libraries. Very brief notes on works dealing with economic geology occupy 64 pages. There is a bibliography of 1261 items, of which just over half relates to mineral resources.

Lovozerskii Shchelochnoi Massiv. [The Lovozero Alkali Massif.] By K. A. Vlasov, M. V. Kuzmenko and E. M. Eskova. Pp. 623, figs. 257. Academy of Sciences, Moscow, 1959. Price, 38r. 25k.

The highly differentiated alkali syenite massif of the Lovozero tundra (Kola peninsula) covers an area of 650 square kilometres, is excellently exposed, and has been studied in great detail by Russian geologists since it was discovered by

W. Ramsay in 1887. This outstanding monograph on the complex is divided into four parts: (1) an account of the geology of the region and of the distribution of the rock-types (pp. 11–74); (2) a description of the pegmatites (pp. 77–238); (3) a memoir on the mineralogy of the rocks (pp. 241–508); and (4) a discussion of the geochemistry and genesis of the deposits (pp. 511–610). The very full studies of this unusual suite of rocks are of special interest in connection with the mineralogy, geochemistry, and economic geology of zirconium, niobium, titanium, the rare earths, thorium, beryllium and gallium. No less than 108 minerals have been identified, eleven of these being new species described in recent Soviet literature. The latter comprise nenadkevichite, karspinskite, vinogradovite, gerasimovskite, seidozerite, belovite, kupletskite, hydrocerite, karnasurtite, berillite and labuntsovite, of which full descriptions are given. Undoubtedly this publication will become a classic in petrological-geochemical literature.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
March 29, 1960

Industrial Minerals and Rocks, 3rd Edit. By JOSEPH L. GILLSON, Editor-in-Chief. Pp. 946; illustrated. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1960. Price, $12.00.

The predecessor (1949) of this edition became such an indispensable reference to everyone connected with the mineral industry that this new up-to-date edition will be highly welcomed. The page size has been increased to 7×10 inches and the format is set in 2 columns. The book has been completely rewritten and considerably enlarged to keep pace with the changes in technology, industrial applications, and usefulness of the industrial minerals. One of the features one notices as he leafs over the pages is the greatly expanded number of well chosen illustrations and charts. Another new feature, and a desirable one, is the increased number of descriptions of mineral deposits. There are four new chapters making the total now 55. A large number of new names are listed among the 62 authors. The selected bibliographies of each chapter are brought up-to-date.

The second edition proved to be an invaluable reference, and this third edition should become even more valuable. Dr. Gillson is to be congratulated for a fine job well done.

Principles of Mineralogy. By WM. H. DENNEN. Pp. 395; figs. 190. Ronald Press Co., New York, 1959. Price, $7.50.

Professor Dennen, of the Massachusetts Institute of Technology, has given us a book that is different from the usual elementary text book of mineralogy. Instead of being devoted entirely to mineral recognition, it is a study of the geometrical, chemical, and physical relationship of matter, using minerals as illustrative examples.

The book is divided into two parts—General Principles, and Mineral Descriptions. In Part I the author discusses symmetry, crystal chemistry, mineralogical relations, physical characteristics of minerals, and chemical testing and mineralogy. The six chapters deal with those phenomena of the solid state of direct concern in mineralogy. It includes also chemical testing, crystallography, and classification of minerals.

Part II covers descriptions of 150 minerals arranged according to mineral

groups. For each mineral are given crystallography, physical properties, occurrence, alteration, other minerals confused with variants, and related minerals. This part furnishes a basis for the students' laboratory identification of mineral specimens.

The book provides students with a mineralogical background that will lead to a knowledge of the solid state. The publishers state that it is "The first elementary text book to present mineralogy as a study of the geochemical, chemical, and physical relationships of all matter." This is a very interesting and worthwhile approach to the elementary study of mineralogy.

The Future of Non-Ferrous Mining in Great Britain and Ireland—A Symposium. Pp. 614; figs. 74; pls. 5. Inst. Mining and Metallurgy, London, 1959. Price, 60s.

The purpose of this symposium was to review the mineralized areas of Great Britain and Ireland and to discuss technical and economic problems bearing on their exploration and development. The symposium also made an appraisal of the potentialities of the industry and discussed means of its revival.

Thirty authors contributed twenty-four papers and they and the accompanying discussions make up this volume.

The subjects covered are the economic geology of the principal mineralized areas, descriptions of mineral districts, discussions of mineral potentialities, mining methods and problems, geophysical prospecting and exploration methods, mineral rights, mining taxation, ownership, and metal prices. Chapters contain a summary of areas of particular interest with recommendations for future action, and a "pattern for the revival of Mineral Exploration in the British Isles."

Many valuable and up-to-date descriptions of mineral deposits are found in the papers and the extended discussions. Throughout the discussions there is a strong feeling that the decline in the flourishing metal industry of a hundred years ago may not be due entirely to exhaustion and that some revival could take place by utilizing modern methods of exploration and a revision of the mining tax structure.

The volume will make a good reference book for anyone interested in the mineral industry of these areas.

Hydrology, 2nd Edit. By C. O. Wisler and E. F. Brater. Pp. 408; figs. 136. John Wiley & Sons, New York, 1959. Price, $9.25.

This new edition has been considerably revised. Two important new chapters have been added. One deals with the hydrologic problems of semiarid regions, written by F. G. Christian and W. J. Parsons, Jr., of the office of the U. S. Army Engineers. The other new chapter on the effect of snow upon the hydrology of an area is by Walter T. Wilson of the U. S. Weather Bureau.

The outstanding features of the book are such problems as determination of spillway and bridge discharge capacities, methods of flood reduction, water conservation, evaluation of the potential power of a river, amounts of water available for water supply or waste disposal on a river. The twelve chapters consider the hydrograph, precipitation, run-off, infiltration, ground water, water losses, floods, and stream-flow records.

This edition is a good up-to-date text and reference book on the subject of hydrology.

BOOKS RECEIVED

ROGER L. AMES AND JOHN E. COTTON

Relation of Ore Deposition to Doming in the North American Cordillera. EDWARD WISSER. Pp. 117; pls. 2; figs. 34; tbls. 3. Geological Society of America Memoir 77, New York, 1960. *Mining districts are discussed in two categories: 1) those whose structural frame is a dome, and 2) those whose structural frame is an anticline. Ore deposition, geographic distribution, and relation of epithermal deposits to Cordilleran development are included.*

Major Activities in the Atomic Energy Programs January–December 1959. Pp. 628; tbls. 15. Price, $2.00. U. S. Atomic Energy Commission, January, 1960. *Contains sections on the atomic energy industry, major activities in the atomic energy programs, and management of radioactive wastes.*

Chemical Composition of Granitic Rocks in Japan. HITOSHI HATTORI and TAMOTSU NOZAWA. Maps 2. Geological Survey of Japan, 1959. *A collection of chemical analyses of Japanese granites. Two pages of English explanation; 217 pages of tables.*

Bulletin Scientifique et Economique du B.R.M.A. No. 5. Bureau de Recherches Minières de l'Algérie, Birmandreis, 1958. Pp. 79; pls. 18, figs. 8; tbls. 7. *Articles on the arsenic and tungsten deposits of Karezas and on the west border of the Beni-Toufout massif. In French.*

Annual Report of the Geological Survey Department for the Year Ended 31st December, 1958. Bechuanaland Protectorate. Pp. 42; tbls. 2; map 1. Price, 3 shillings. *Results of mineral investigations are reported for coal, asbestos, and manganese, and geological mapping is presented.*

5th Inter-Guiana Geological Conference Addresses to the Opening Session. Pp. 11. British Guiana Geological Survey, Georgetown, 1959.

Radiometrische Bestimmungen an Mineralien und Gesteinen (Grundlagen, Messverfahren mit Zählrohr, Eichung und Anwendung). KLAUS ROTHE. Pp. 159; figs. 63; tbls 9. Freiberger Forschungshefte C 68 Geophysik. Akademie-Verlag, Berlin, August, 1959. *A detailed presentation of the theory, methods of measurement with various counting devices, calibration, and use of radioactive material and data.*

Annotated Bibliography of Papers Related to the Geology of Idaho 1949–1957. C. P. Ross. Pp. 219. Idaho Bureau of Mines and Geology Pamphlet 119, Moscow, 1959.

Carboniferous System of Japan. Pp. 65; figs. 12. Geological Survey of Japan Special Report D, Hisamoto-chô, Kawasaki-shi, 1960. *The Carboniferous rocks are classified into 8 lithogenic units with several diastrophisms recorded.*

The Cenozoic Turritellidae of Japan. TAMIO KOTAKA. Pp. 135; pls. 15; figs. 2. The Science Reports of the Tohoku University, Sendai, Japan, Second Series (Geology). Vol. XXI, No. 2, 1959. *Complete classification and description of taxonomic categories a.e proposed.*

A geologia e o desenvolvimento económico e social de Moçambique. ANTÓNIO J. DE FREITAS. Pp. 396; pls. 23; figs. 5; tbls. 13. Colored geologic map scale 1 inch: 50 cm. Province of Mozambique, Lourenço Marques, 1959.

Progress Report on Clays of Montana. U. M. SAHINEN, R. I. SMITH, and D. C. LAWSON. Pp. 83; figs. 2; tbls. 7. Montana Bureau of Mines and Geology Bull. 13, Butte, 1960. *This study catalogs the clay and shale deposits of the state.*

Annual Water-Level Measurements in Observation Wells, 1951–1955, and Atlas of Maps Showing Changes in Water Levels for Various Periods from Beginning of Record Through 1954, New Mexico. H. O. REEDER and others. U. S. Geological Survey, pp. 339; figs. 161; tbls. 26. Technical Report 13, State of New Mexico, State Engineer Office, Santa Fe, 1959. *Ground-water levels in the areas studied have declined in most cases since 1941, reflecting the increased use of irrigation and below average rainfall.*

Geological Reconnaissance of the Area Between Kristiansand and Lillesand. R. V. DEITRICH. Pp. 78; figs. 2. Norges Geologiske Undersökelse, Nr. 205, Oslo, 1959. *Rocks of greenschist and epidote-amphibolite facies are present and the diverse banded gneisses are discussed.*

Boletin de la Universidad Nacional de Ingenieria, Serie IV, Tomo XXXII, Julio, Agosto, y Setiembre de 1959. Pp. 89. Peru. *Report on a forum about the energy problems of Peru includes the mineralogy and treatment of coal.*

Geological Interpretation of Aeromagnetic Maps. A. A. SOCOLOW. Inform. Circ. Nos. 24–35. Pennsylvania Geological Survey, Harrisburg, 1959. *Brief discussions of bedrock and causes of magnetic anomalies; attributed to gneisses, diabases, magnetite bands in gneiss, wissahickon schist, old iron mines, and the new Grace Mine.*

Structure and Origin of Some Uranium-Bearing Veins in Portugal. J. CAMERON. Pp. 56; figs. 13. Junta de Energia Nuclear, Lisboa, 1959. *Uranium vein deposits are found in the north-central part of Portugal in Hercynian granites.*

The Distribution of Halogens in Skarn Amphiboles in Central Sweden. PER GEIJER. Pp. 23; tbls. 2. Arkiv för Mineralogi Och Geologi, Band 2, nr 36, Stockholm, 1960. *Occurrences of amphiboles previously designated "reaction skarns" contain fluorine in amounts comparable to those in the pyrometasomatic skarns.*

Twelfth Annual Report of the Joint Coal Board for the Financial Year 1958–1959. Pp. 132; tbls. 32; photos 14. Hobart, Tasmania, 1959. *Contains general review of the industry, coal production, conservation and working of coal resources, marketing, and welfare.*

Graptolite Faunas of the Marathon Region, West Texas. W. B. N. BERRY. Pp. 179; pls. 17; figs. 3; index map. Price, $3.00. Bureau of Economic Geology, The University of Texas, Austin, 1960. *This study establishes a standard section against which other graptolite-bearing formations may be compared. Correlations are made between North America, Great Britain and Australia.*

Directory of Washington Mining Operations 1959. G. W. THORSEN. Pp. 78; pl. 2. State of Washington Division of Mines and Geology, Inform. Circ. 34, Olympia, 1960.

Virginia Mineral Localities 1960 Edition. R. V. DIETRICH. Pp. 84. Bull. of the Virginia Polytechnic Institute, Vol. LIII, No. 7, May, 1960.

California Division of Mines—San Francisco, 1959.

Special Rept. 58. Geology of Limestone and Dolomite Deposits in the Southern Half of Standard Quadrangle Tuolumne County, California. E. W. HART. Pp. 25; pls. 3; figs. 2; photos 19; tbls. 3. Price, 75 cents. *Eleven deposits of high-calcium limestone and five deposits of high-magnesium dolomite exist and appear to be suitable for industrial use.*

Special Rept. 60. Tertiary Volcanic Domes Near Jackson, California. R. L. ROSE. Pp. 21; pls. 11; figs. 4; tbls. 2. Price, 50 cents. *Five volcanic mass exhibits are structurally similar and consist of flow banded felsophyre and breccia.*

Geological Survey of Canada—Ottawa, 1959–1960.

Bull. 53. The Oxfordian Beds of the Jurassic Fernie Group, Alberta and British Columbia. HANS FREBOLD, E. MOUNTJOY, and RUTH REED. Pp. 47; tbls. 2; pls. 12; figs. 6. Price, $1.00. *In this paper all information on the distinctive Oxfordian beds is assembled—the general nature and fauna by Frebold, the stratigraphy of the northern exposures by Mountjoy, and the subsurface information by Miss Reed.*

Bull. 56. Contributions to Canadian Palynology No. 2. J. TERASMAE. Pp. 41; pls. 6; figs. 20; tbls. 3. Price, 50 cents. *Through pollen studies correlation of terraces on either side of the St. Lawrence River may be made.*

Paper 59-8. Surficial Geology of the Becancour Map-Area, Quebec. N. R. GADD. Pp. 34; tbls. 1. Map 42-1959, Scale 1:63,360. Price, 50 cents. *Some sands seem to be good aquifers. Varved clays are used in the brick industry. Iron-enriched muck and peat have been burned to obtain iron oxides for paint pigments.*

Memoir 305. Elbow-Heming Lakes Area Manitoba. J. C. MCGLYNN. Pp. 72; pls. 2; tbls. 10. Price, 75 cents. *Petrographic studies show six granites to be present, some intrusive and others the product of granitization.*

Aeromagnetic Maps, scale 1/63,360. Maps nos. 5929, 766g, 770g, 772g, 777–781g, 783g, 786–787g. Musquash, Bay of Fundy, N. B.; Granville Ferry and Centerville, N. S.; Salmon River and Waterford, N. B.; Owl's Head, Tangier, Upper Musquodoboit, Margaretsville, Shubenacadie and Truro, N. S. Maps nos. 900g–909g, Ontario—St. Raphael, Lindbergh, Blackstone, Obaskaka, Gitche, Upturnedroot, Hinton, Stirland, Yoyoy, and Weagamow Lakes; Geologic maps (in color) of Cape Canso (104A) and Louisburg (1088A), Nova Scotia; Map 55-1959, Geology Hobart Id., N.W. Territories, scale 1/253,440.

National Advisory Committee on Research in the Geological Sciences, Ninth Annual Report 1958–59. Pp. 216. Price, 50 cents. *Includes a yearly review, subcommittee reports, research project summaries, research grants, and listing of current research in the geological sciences in Canada, 1958–59.*

Geological Survey of Fiji—Suva, 1959.

Bull. 2. Geology of the Lautoka Area, North-West Viti Levu. R. W. BARTHOLOMEW. Pp. 25; pls. 9; tbls. 1; map 1. Price, 12s. 6d. *Laterites, basaltic volcanics, andesite extrusives, and propylitized endesites are the four major rock types.*

Bull. 3. Regional Geology of Lomawai-Momi Nandroga, Viti Levu. R. E. HOUTZ. Pp. 20; pls. 14; map 1. Price, 12s. 6d. *Eight base metal prospects have been located during regional mapping of the granite intrusive terrain.*

Forschungsberichte des Landes Nordrhein-Westfalen, 1959–1960.

Nr. 696. Massenspektrometrische Untersuchungen an Bleierzen. HANS EHRENBERG and HANS J. MÜRTZ. Pp. 32; figs. 12; tbls. 2. Price, DM 9.40. *A discussion of mass spectrometric measurements of lead.*

Nr. 760. Vergleich von Korona- und Hitzdrahtanemometer durch Messung von Turbulenzspektren. BRUNO FRANZEN, WILHELM FUCKS, and GEORG SCHMITZ. Pp. 70; figs. 49. Price, DM 19.90.

Nr. 782. Temperatur- und Dehnungsmessungen in einem Gefrierschacht. KARL WERNER. Pp. 82; figs. 49; tbls. 8. Price, DM 25.30. *A report on temperature and plastic flow measurements in a frozen hole with a discussion of methods of measurement and reliability of data.*

Institute for Geology and Subsurface Research—Athens, Greece, 1959–1960.

Vol. V, No. 3. Das Braunkohlebecken von Megalopolis. von G. Marinos, J. Anastopoulos, and N. Papanikolaou. Pp. 51; figs. 11, tbls. 5. *German summaries. Articles on stratigraphy of the brown coals of Megalopolis and on the geophysical measurements in the brown coal.*

Vol. VI, No. 1. Griechenlands Feuerfeste Gesteine. von G. Marinos, and G. Mastrantonis. Pp. 82; pls. 30; tbls. 27. English abstract. *The possibility of an operating refractory ceramic industry in Greece is discussed; if organized it would be able to utilize at least 80% indigenous raw material.*

Illinois Geological Survey—Urbana, 1960.

Circ. 284. Salem Limestone in Southwestern Illinois. J. W. Baxter. Pp. 32; figs. 8; tbls. 3. *The Salem limestone is subdivided into the Kidd, Fults, Chalfin, and Rocher Members.*

Circ. 285. Classification of the Wisconsinian Stage in the Lake Michigan Glacial Lobe. J. C. Frye and H. B. Willman. Pp. 16; fig. 1; 4 measured geologic sections. *A revised time-stratigraphic classification of the Wisconsinian Stage of the Lake Michigan lobe is presented; also new rock-stratigraphic names are introduced.*

Circ. 286. Clay Mineralogy of Pre-Pennsylvanian Sandstones and Shales of the Illinois Basin. Pt. 1—Relation of Permeability to Clay Mineral Suites. T. W. Smoot. Pp. 20; figs. 8; tbls. 5. *The heterogeneity of clay mineral suites in sandstones is brought about by degradation, by circulating formation fluids, low permeability of shales, the circulation and consequent degradation.*

Circ. 287. Clay Mineralogy of Pre-Pennsylvanian Sandstones and Shales of the Illinois Basin. Pt. II—Clay Mineral Variations Between Oil-Bearing and Non-Oil-Bearing Sandstones. T. W. Smoot and Kedar Narain. Pp. 14; figs. 4; tbls. 2. *Clay mineralogy differences between two types of sandstone are thought to be partly a function of the presence or absence of hydrocarbons.*

Circ. 288. Solvent Extract and the Plastic Properties of Coal. E. D. Pierron and O. W. Rees. Pp. 11; figs. 4; tbls. 5. *For each solvent yields of extracts are proportional, but not necessarily directly proportional, to fluidities of the coals.*

Circ. 289. Effect of High-Carbon Components and Other Additives on the Character of Cokes. Laboratory-Scale Study. J. A. Harrison. Pp. 29; figs. 16; tbls. 5. *Mixtures of a standard coal sample with fusain, anthracite, coke dust, petroleum coke, black shale, and a benzene extract of coal tar pitch produced cokes of higher quality than coke made from the standard sample alone.*

Circ. 290. Lightweight Aggregate from Illinois Shales. W. A. White. Pp. 29; pls. 2; figs. 2; tbls. 2. *A study of the mechanism of bloating shales and to determine which shales are self-bloating and which require special agents.*

Circ. 291. Fluid Flow in Petroleum Reservoirs. III.—Effect of Fluid-Fluid Interfacial Boundary Condition. Walter Rose. Pp. 18; figs. 9. *It is suggested that a flowing fluid has more mobility when in contact with an immiscible fluid. Lubrication effect is increased if the viscosity ratio of the two fluids has a low value.*

Rept. of Investigations 213. Ground-Water Geology of Winnebago County, Illinois. J. E. Hackett. Pp. 63; pls. 2; figs. 11. *Four geohydrologic units were noted: glacial drift aquifers, Ordovician dolomite aquifers, and sandstone aquifers of Ordovician age and Cambrian age.*

Kansas Geological Survey—Lawrence, 1959–1960.

Bull. 134, Pt. 8. Marine Bank Development in Plattsburg Limestone (Pennsylvanian), Neodesha-Fredonia Area, Kansas. J. W. HARBAUGH. Pp. 289–331; pls. 13; figs. 3; tbl. 1. *A study of the Plattsburg Limestone in southeastern Kansas was made from outcrops and 200 drillers logs.*

Bull. 142, Pt. 1. Dakota Formation Refractory Clays and Silts in Kansas. NORMAN PLUMMER, M. P. BAULEKE, and W. B. HLADIK. Pp. 52; figs. 5; pls. 9. *Bricks made of the refractory clays of the Dakota formation show excellent high-temperature volume stability and hot load deformation characteristics.*

Miscellaneous Report. Research and Activities of State Geological Survey of Kansas Fiscal Year Ending June 30, 1959. GRACE MUILENBURG. Pp. 39.

Province of Manitoba Department of Mines and Natural Resources—Winnipeg, 1959.

Publ. 58-1. Mississippian Stratigraphy of Manitoba. H. R MCCABE. Pp. 99; figs. 26; cross-sections 4; maps 12. *The descriptive and interpretive stratigraphy are presented and the petroleum prospects are discussed. This study is based entirely on well logs inasmuch as the Mississippian rocks do not outcrop anywhere in Manitoba.*

Publ. 58-2. Gypsum-Anhydrite Deposits of Manitoba. B. B. BANNATYNE. Pp. 46; tbls. 2; figs. 8; pls. 2. *The geology of the gypsum deposits at Amaranth and Gypsumville is reported.*

Publ. 58-3. Geology of the Oxford House-Knee Lake Area Oxford Lake and Gods Lake Mining Divisions. G. S. BARRY. Pp. 39; fig. 1; maps, scale 1 inch: 1 mile. *The volcanic and sedimentary rocks are divided into two groups, separated by an unconformity. All the rocks have undergone low- to medium-grade metamorphism.*

Northern Rhodesia Geological Survey—Lusaka, 1960.

Bull. 4. The Karroo System and Coal Resources of the Gwembe District, South-West Section. R. TAVENER-SMITH. Pp. 84; pls. 17; tbls. 11. 2 maps, scale 1:125,000. Price £1 10s. *The lithology and stratigraphy of the Karroo rocks in the mid-Zambesi valley are described and a correlation is made with similar rocks in Southern Rhodesia.*

Mineral Map of Northern Rhodesia. Scale, 1 inch: 75 km. *Yearly production graphs for copper, zinc, lead, vanadium, and cobalt.*

South Dakota Geological Survey—Vermillion, 1960.

Minerals Rept. 6. Mineral Production in South Dakota in 1959. A. F. AGNEW. Pp. 7; fig. 1; tbl. 1.

Geologic maps, scale 1/62,600, in color, with text on back of the following quadrangles: Hartford, Chester, Dallas, Martin, Okreek, Sioux Falls, and Dell Rapids; Oil and Gas Investigations maps 3 and 4, magnetometer and oil test maps.

Ontario Department of Mines—Toronto, 1960.

Vol. LXIX, Pt. 4, 1960. Geology of the Bennett-Tanner Area. W. L. YOUNG. Pp. 16; photos 4; maps, scale 1 inch: ½ mile. *Discovery of a massive sulfide deposit 3 miles west of Bennett Township led to present geologic mapping.*

Vol. LXIX, Pt. 5, 1960. Geology of the Lumby Lake Area. R. S. WOOLVERTON. Pp. 52; maps, scale 1 inch: ½ mile; photos 12. *The area mapped is part of the greenstone belt with some adjacent granitic rocks.*

Quebec Department of Mines, Quebec—1959–1960.

Geological Rept. 86. Rohault Area Abitibi-East and Roberval Electoral Districts. J.-E. GILBERT. Pp. 31; pls. 2; map 1. *Considerable mineral exploration has been carried out in the northern part of the area and an important gold-copper deposit was discovered.*

Geological Rept. 87. Hazeur-Druillettes Area Abitibi-East Electoral District. A.-N. DELAND and P.-E. GRENIER. Pp. 71; pls. 6; figs. 2; maps. 3. *This study in the region south of the Chibougamou region concerns the relation between Keewatin- and Grenville-type rocks.*

Geological Rept. 88. Chaste-Mazarin Area Abitibi-East Electoral District. MARCEL TIPHANE. Pp. 15; pls. 4; tbl. 1. Map 1244; scale, 1:63,360. *A magnetic anomaly has been outlined, but the cause of it is not known. Limited occurrences of chrysotile warrants further exploration.*

Geological Rept. 89. Céloron-Carquevile Area Abitibi-East and Abitibi-West Electoral Districts. S. H. Ross. Pp. 18; pls. 2; tbl. 1. Map 1243; scale, 1:63,360. *Some sulfides have been found in silicified schists and tuffs.*

Outline of Progress of the Mining Industry in the Province of Quebec during the Year 1959. EDGAR-E. BÉRUBÉ.

List of the Principal Operators and Owners of Mines and Quarries in the Province of Quebec. Pp. 94 with a 32 page supplement replacing the one issued in 1959.

Virginia Department of Conservation and Economic Development—Charlottesville, 1959–1960.

Information Circ. 1. Catalog of Oil and Gas Wells in Well Sample Repository on August 1, 1959. D. C. LE VAN, compilator. Pp. 11. *Listing of test wells drilled for oil and gas exploration in Virginia for which the Virginia Division of Natural Resources has cores on file.*

Mineral Resources Report 1. Sources of Aggregate Used in Virginia Highway Construction. E. O. GOOCH, R. S. WOOD, and W. T. PARROTT. Pp. 65; pls. 10. *Aggregate is classified into three grades on the basis of abrasion loss, specific gravity, and absorption.*

Western Australia Geological Survey—Perth, 1958–1959.

Bull. 6. The Gypsum Deposits of Western Australia. L. E. DE LA HUNTY and G. H. Low. Pp. 110; pls. 6; figs. 2; tbls. 7. *Information on mineralogy, chemistry, geology, and mining methods of all the gypsum deposits.*

Bull. 112. Miscellaneous Reports for 1955. *Seventeen reports of economic interest including articles on gold shows, uranium deposits, ground-water, graphite deposits, and petroleum exploration.*

Economic Geology
Vol. 55, 1960, pp. 861–862

SCIENTIFIC NOTES AND NEWS

The D. C. Jackling Post Doctoral Fellowship has been awarded to JOHN LAWRENCE MERO, Doctor of Engineering, from the University of California, Berkeley, who will work under the direction of Professor L. E. Shaffer, Professor of Mining at Berkeley. His project will be to investigate more fully the occurrence, cause, distribution, composition, and environment of deep-sea manganese nodules containing nickel, cobalt, and copper, the knowledge of which has been extended during the Geophysical Year.

JOHN GITTINS has been awarded the Peacock Memorial Prize (1959) of $200 by the Walker Mineralogical Club. The prize is awarded to the graduate student submitting the best scientific paper on pure or applied mineralogy, including crystallography, mineralogy, petrology, ore genesis, and geochemistry.

ROY W. PHENDLER, JR., formerly Mine Geologist with the Cerro de Pasco Corporation, has recently been transferred to Lima, Peru, where he will work in the Corporation's Exploration Department.

FRANCIS CAMERON has succeeded Andrew Fletcher as president of St. Joseph Lead Co.

RICHARD G. BOWEN has joined the staff of the Oregon Department of Geology and Minerals Industries as a geologist. He has been assigned to the Department's field project on copper occurrences in Oregon.

FRED W. STRANDBERG, chief mining engineer for the Anaconda Co. in Butte, has retired after a 43-year career in the mining field.

WILLIAM H. SWAYNE has been appointed chief geologist of the Anaconda Company's South American Division. Prior to this Mr. Swayne had been for four years chief geologist with the Chile Exploration Co. with headquarters at Chuquicamata, Chile.

W. W. RUBEY is resigning from the U. S. Geological Survey to accept a research professorship at the University of California in Los Angeles.

W. E. WRATHER has returned to his Washington home after a winter in Florida.

HOWLAND BANCROFT has retired from the board of directors of Cerro de Pasco Corp. after serving there since 1950.

COOPER H. WAYMAN was promoted recently from senior technologist to supervisor of petrography and mineral technology research, Applied Research Laboratory, U. S. Steel Corp., Monroeville, Penna.

ARTHUR H. BROWNLOW has been made an assistant professor of geology at the Missouri School of Mines & Metallurgy. He received his Ph.D. in geology from M.I.T. in February of 1960.

JOHN K. GUSTAFSON, a member of the U. S. Atomic Energy Commission since 1947, was among 12 outstanding Washington University alumni to receive alumni federation citations at Founders Day ceremonies on February 21.

ERNEST L. OHLE, who since 1957 has been Chief Geologist of the Copper Range Company and its subsidiary, the White Pine Copper Company, has been named Vice President—Exploration of the Copper Range Company. His headquarters will continue to be located at White Pine, Michigan.

HAROLD W. OWENS, district geologist for the Humble Oil and Refining Company at Tallahassee, Florida; is winner of the George C. Matson Award of the American Association of Petroleum Geologists for the excellent presentation of his paper entitled "Florida-Bahama Platform" at the 45th annual meeting of the AAPG held in Atlantic City, New Jersey, April 25–28, 1960.

The MASSACHUSETTS INSTITUTE OF TECHNOLOGY has received a gift of $1,250,000 from the Texas Instruments Company founder and his wife to establish Earth Sciences scholarships for students from Texas or other states of the Southwest.

ROBERT C. BRYANT has set up a consulting service in Fairbanks to serve all of the interior of Alaska, offering services in geological engineering, groundwater geology, mining geology, and in exploration of minerals and petroleum.

DAVID WILLIAMS, Professor of Mining Geology and Head of the Department of Geology, Royal School of Mines, Imperial College of Science and Technology, London, was inducted in May as President of the Institution of Mining and Metallurgy for 1960–61 and delivered his Presidential Address on "Progress in Mining Geology: Training, Research and Development."

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